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OBSERVATIONS ON THE SORPTION OF ORANGE II BY WOOL[1]

BY JOAN KRUGER[2], R. DONOVAN[2], AND P. LAROSE[2]

ABSTRACT

The sorption of Orange II by wool has been determined at 100°C. in the presence of acetic acid and of phosphoric acid. The results are compared with those obtained with sulphuric acid solutions. The sorption isotherms found are represented by the same form of equation as had been found previously for sulphuric acid and for hydrochloric acid solutions. Determinations made with low dye concentrations indicate that the complete isotherms are S-shaped and that the first portion of the curve can be represented by an equation of the Freundlich type. Some of the factors controlling the sorption of the dye are discussed.

INTRODUCTION

In a previous paper (1) it was shown that the curves representing the sorption of Orange II by wool at 100°C. in solutions containing sulphuric acid or hydrochloric acid did not follow strictly the course of a Langmuir adsorption isotherm although it had the same general appearance. It was found however, that the relation between the amount of dye sorbed by the wool and the concentration of the dye in solution at equilibrium could be expressed satisfactorily by an equation of the Langmuir type if the activity of the dye in solution was made proportional to its concentration raised to a power greater than one. To determine whether acids other than sulphuric or hydrochloric gave a similar relationship, the sorption of the dye by wool from solutions containing acetic acid or phosphoric acid was measured. For purpose of comparison, some of the previous determinations with sulphuric acid solutions were repeated.

It was also noticed in the earlier experiments that for very low dye concentrations, the sorption curve appeared to be of a different form from that for the higher concentrations. This part of the sorption isotherm was investigated further by carrying out sorption measurements with lower concentrations of dye than had been used in our earlier experiments.

METHODS

The experiments were carried out as described previously (1). Briefly, a known weight of wool, previously extracted with alcohol and with ether and equilibrated to a pH of 5.5 was boiled in a solution containing a known amount of dye and acid for one and one-half hours, a reflux condenser being used to prevent

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undue loss of liquid during the boiling. The amount of dye sorbed by the wool was determined by measuring colorimetrically the change in dye concentration after equilibrium had been reached. Measurement of pH with a glass electrode was carried out as before.

RESULTS

The results of the sorption experiments carried out for the purpose of comparing the action of acetic acid and of phosphoric acid with that of sulphuric acid are given in Table I, while Fig. I illustrates the relation between the amount of dye sorbed and the dye concentration in the solution at equilibrium for three of the acid solutions chosen so as to give a saturation value of the same order.

TABLE I

SORPTION OF ORANGE II IN ACID SOLUTIONS *

0·016 *N* acetic			0·044 *N* acetic			0·80 *N* acetic		
C_B**	C_F***	pH†	C_B	C_F	pH	C_B	C_F	pH
0·044	·085	3·91	0·032	0·108	3·49	0·017	0·086	2·44
0·337	·198	4·24	0·085	0·160	3·61	0·051	0·215	2·55
1·057	·287	4·39	0·144	0·212	3·72	0·214	0·405	2·73
2·071	·316	4·47	0·251	0·260	3·81	0·778	0·608	2·84
			0·421	0·305	3·88	1·145	0·674	2·88
			0·664	0·347	3·92	2·570	0·722	2·88
			0·988	0·383	3·97	5·00	0·799	2·88
			1·400	0·414	3·99			
			1·872	0·442	4·02			

0·02 *N* phosphoric			0·0074 *N* sulphuric			0·0047 *N* sulphuric		
C_B	C_F	pH	C_B	C_F	pH	C_B	C_F	pH
0·050	0·111	2·73	0·068	0·075	3·20	0·133	0·106	3·67
0·086	0·164	2·81	0·094	0·107	3·23	0·243	0·157	3·79
0·110	0·217	2·91	0·207	0·208	3·31	0·397	0·205	3·88
0·147	0·266	3·08	0·292	0·258	3·38	0·525	0·220	3·93
0·161	0·326	3·29	0·418	0·306	3·42	0·738	0·241	4·09
0·407	0·368	3·58	0·628	0·349	3·51	1·410	0·260	4·27
0·980	0·391	3·89	0·996	0·383	3·68	2·295	0·266	4·50
1·846	0·397	4·08	1·564	0·406	3·81			
2·665	0·406	4·21						

* The acid concentrations given are those initially present in the dye solution.
** C_B = milliequivalents of dye per liter of solution at equilibrium.
*** C_F = milliequivalents of dye sorbed per gram of wool.
† The pH values are those for the dye solution after sorption of the dye.

The results of the tests carried out with low dye concentrations in sulphuric acid solutions of two different concentrations are given in the form of sorption curves in Fig. 2.

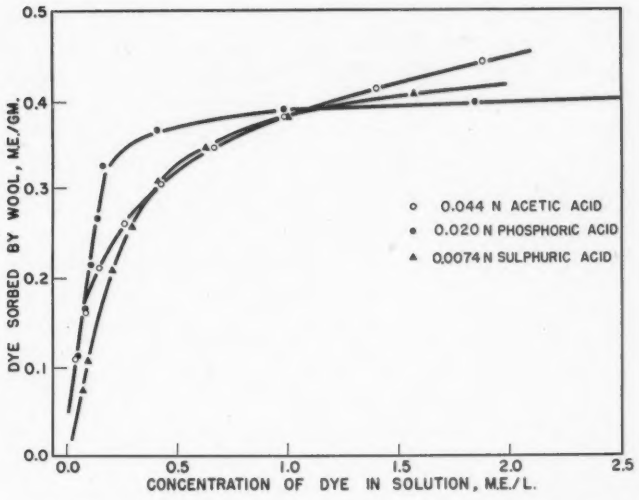

FIG. 1. Sorption isotherms for Orange II in three different acid solutions.

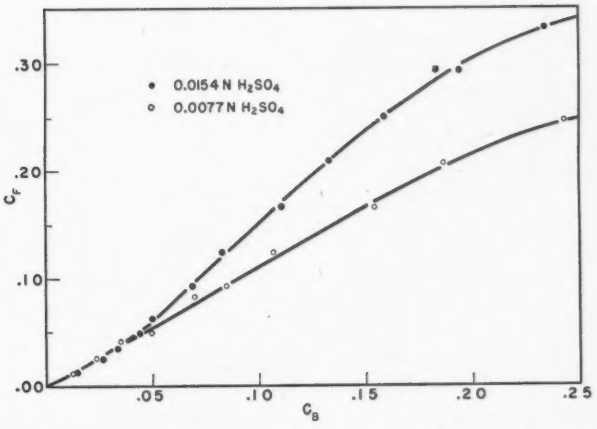

FIG. 2. Sorption isotherms for low concentrations of Orange II in sulphuric acid solutions.

DISCUSSION

Several noteworthy points arise from the results. In the first place the three acids investigated produce different sorption effects quite apart from those to be expected from the difference in pH of the solutions. The pH of the phosphoric acid solution was lower at the low dye concentration and higher at the high dye concentrations than the pH of the other two acids with which it has been compared in Fig. 1. It is to be expected therefore that the amount of dye sorbed from the phosphoric acid solution would be higher at the low dye concentrations and lower at the high concentrations than that sorbed from the other two acid solutions. However, it is evident from an examination of Table I that other factors also affect the sorption. For instance the dye sorbed was 0.368 m.e. for a dye concentration of 0.407 m.e. per liter in phosphoric acid solution of pH 3.58, whereas in the sulphuric acid (0.0074 *N*) with a pH 3.51, a dye concentration of 0.628 m.e. per liter is required to give a sorption of 0.349 m.e. If one compares the results of the 0.044*N* acetic acid solution with those obtained with the 0.0074*N* sulphuric acid solution, the dye sorption from the acetic acid solution is found to be practically the same as that from the sulphuric acid solution although the pH is higher in the former. For example one can compare directly the sorption of 0.305 m.e. at the pH 3.88 from the 0.044*N* acetic acid solution with a similar sorption value obtained at pH 3.42 from the sulphuric acid solution.

Another factor which affects the dye uptake by the wool is competition from the acid anion. This effect is more difficult to evaluate since it depends both on the concentration of the anion in question and its affinity for the wool. According to Steinhardt, Fugitt, and Harris (7) the affinity of acetic acid is less than that of sulphuric acid at pH values corresponding to those reached in our experiments. Moreover the concentration of the acetate ion is also much less than that of the sulphate ion at these pH values. One would expect the sorption of the dye to be higher therefore in acetic acid solution than in sulphuric acid solution of comparative pH. For similar reasons one would expect the dye sorption to be also higher in the presence of phosphoric acid than in the presence of sulphuric acid of comparative strength. Our experimental results are in accord with this view.

The degree of swelling of the wool might also be expected to exert some influence on the amount of dye sorbed but there is not sufficient information available in the literature to enable one to make a study of the comparative effects of swelling caused by acetic, sulphuric, and phosphoric acids under the conditions of our dyeing experiments.

The large change in pH of the phosphoric acid solution, as more and more dye is added to, and sorbed from, the solution, is partly due to a buffering action of the phosphate ions which become more and more in excess as dye anions are sorbed by the wool. A reduction in the ionization of the acid also takes place, but to a lesser extent, with acetic acid and with sulphuric acid.

Another difference in behavior between that of the acetic acid solutions and that of the other acids is observed when the equation $C_B^n/C_F = \alpha + \beta C_B^n$ is applied to the present results. This is the equation found previously to express

the dye sorption results when sulphuric acid or hydrochloric acid was used in the dye solution (1). C_B and C_F have the same meaning as in Table I, while α, β, and n are constants which vary with the concentration and nature of the acid used. Whereas n had been found to be greater than one for sulphuric acid and for hydrochloric acid, the acetic acid solutions are now found to yield values of less than one for the exponent.

The values of n together with the calculated values of C_F (max), the maximum combining capacity of wool under the conditions of the experiments, are given in Table II.

TABLE II

VALUES OF n AND C_F (MAX) FOR THE VARIOUS ACID SOLUTIONS

Acid	n	C_F (max), m.e./gm.
0·0047 *N* sulphuric	1·48	0·272
·0074 *N* sulphuric	1·37	0·437
·02 *N* phosphoric	1·40	0·405
·016 *N* acetic	0·80	0·342
·044 *N* acetic	0·58	0·640
·80 *N* acetic	0·89	0·826

The equation $C_B^n/C_F = \alpha + \beta C_B^n$ can be written in another form $\frac{\theta}{1-\theta} = AC_B^n$, where $\theta = \frac{C_F}{C_F \text{ (max)}}$ and A is a constant $= \frac{1}{\alpha C_F \text{ (max)}}$. This relation is illustrated in Fig. 3 where $\frac{\theta}{1-\theta}$ is plotted against C_B^n for the 0.044*N* acetic acid results. It was suggested in an earlier paper (1) that a possible reason for the value of n being greater than one was an apparent increase in the maxi-

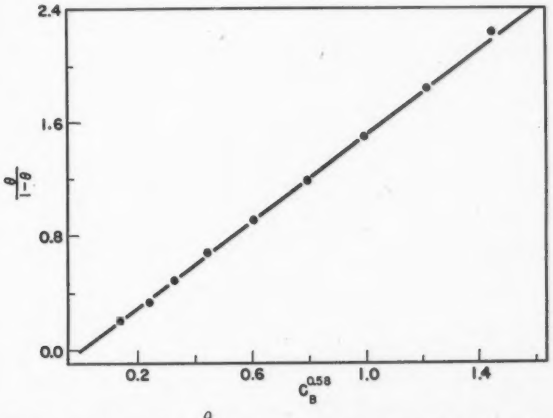

FIG. 3. Test of the equation $\frac{\theta}{1-\theta} = AC_B^n$ for the 0·044 *N* acetic acid solution.

mum combining capacity of wool as the amount of dye sorbed increases. Some evidence for this will be presented in a subsequent paper. If this explanation is correct a value of n less than one should indicate a diminishing combining effect with increased dye sorbed. Preliminary experiments have shown indeed that the relation between amount of dye sorbed and acid taken up by the wool for acetic acid solutions is different from that found with sulphuric acid and with hydrochloric acid.

Another point of interest in the results reported here is the shape of the sorption curve for low dye concentrations. Fig. 2 shows the sorption curves obtained at 100°C. with sulphuric acid of two different concentrations. The initial part of the curve is convex to the dye concentration axis although the curvature is not very pronounced for the results obtained with the less concentrated acid solution. For practical purposes the latter results may be considered as lying on a straight line up to a concentration of 0.20 m.e. per liter. By plotting log C_F against log C_B, a straight line is obtained for the initial points as shown in Fig. 4 where the results for the 0.0154N sulphuric acid solution are

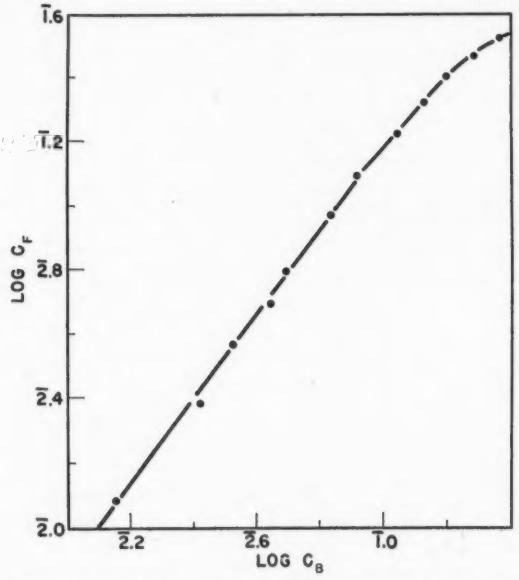

FIG. 4. Logarithmic plot of the results for the 0·0154 N sulphuric acid solution as a test of the Freundlich equation.

plotted in this way. The equation for this part of the sorption isotherm is found to be $C_F = 3.05\ C_B^{1.30}$, and for the less concentrated acid it is $C_F = 1.35\ C_B^{1.07}$. The relation holds up to a concentration C_B of about 0.10 m.e. per liter. The entire sorption curve is therefore S-shaped and may be compared to the isotherm for gaseous adsorption known as the type V isotherm. In fact it is possible to use

the equation given by Brunauer (2) for this type of curve and by a proper choice of constants fit it to the curve of Fig. 2. This would appear to indicate an interaction between the sorbed dye molecules. The following considerations support this view. If the data of Speakman, Stott, and Chang (6) for the swelling of wool, which they measured at temperatures up to 70°C., are extrapolated to 100°C., one obtains about 38% swelling and this corresponds to about 0.30 cc. increase in volume per gram of wool. If one assumes a volume of 400 $Å^3$ for the dye molecule and if the dye were to fill the whole available volume, there would be room for 1.25 m.e. of dye in 1 gm. of wool. However, it is unlikely that all the space accessible to water is also available to the large dye molecule and this figure is undoubtedly too high unless the attractive force for the dye is so large that the dye produces a greater swelling action than that of water alone. Long before the wool is saturated with the dye therefore, there must be a large percentage of the dye molecules that are so close to each other that they interact. One can also proceed from the free surface that has been calculated for wool and arrive at a similar conclusion. Speakman (5) has calculated the internal surface of micelles to be roughly 1×10^6 sq. cm. per gm. while Rowen and Blaine (4) by applying the B.E.T. equation to the water sorption isotherm found a surface of 2×10^6 sq. cm. per gm. Using the latter figure one finds that this surface could accommodate 0.32 — 1.28 m.e. of dye depending on the orientation of the dye molecule. This reasoning also implies that all space available to water becomes available to the dye molecules. It seems therefore that when wool sorbs large amounts of dye the dye molecules must lie within the field of attraction of the neighboring molecules. It is not surprising then to find that the sorption of dyes does not obey relationships such as that of Gilbert and Rideal (3) or that the isotherm is not of the Langmuir type.

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THE OXIDATION, DECOMPOSITION, IGNITION, AND DETONATION OF FUEL VAPORS AND GASES

XXI. NUCLEAR IGNITION AS ILLUSTRATED BY THE CHARACTERISTICS OF COMPRESSION AND SPARK IGNITION; PENTANE, HEXANE, AND HEPTANE AS ENGINE FUELS[1]

By R. O. King[2], E. J. Durand[3], A. B. Allan[4], E. J. T. Hansen[5], and V. E. Bowen[5]

ABSTRACT

Experiments made with acetaldehyde and diethyl ether as fuels for the C.F.R. carburetor type engine, described in Parts XIX and XX, supported the view that autoignition of the end gas as indicated by knocking combustion was due to a decomposition reaction in the fuel which provided nuclei of ignition. The compression ratio, in the special conditions of the experiments, could be raised to obtain autoignition before t.d.c. The engine could then be run without spark ignition. The timing of autoignition could be varied as required to obtain maximum values of power and thermal efficiency at any particular mixture strength, by adjustment of compression ratio to a corresponding optimum value. The essential features of the special conditions were a subnormal charge density, required to prevent unduly severe combustion knock as mixture strength approached and then exceeded the correct value and relatively low surface temperatures in the combustion chamber as required to prevent the formation of products of surface oxidation at an appreciable rate. The engine then became a compression ignition machine which differed from the conventional single stroke variety in having an exhaust valve and also in the fact that ignition delay occurred necessarily during compression instead of being reckoned as beginning on its completion. It is therefore of interest that characteristics of ignition by compression as determined by the engine experiments of this Part are in agreement with those determined by experiments with the M.I.T. single stroke rapid compression machine, in so far as comparable experiments have been carried out. Experiments made in the "special" conditions and with nearly normal varieties of heptane, hexane, and pentane are described in this Part. Compression ratio was always adjusted to the value for which power output was a maximum. This value is described as the optimum compression ratio (Opt. C.R.). The method of determination of Opt. C.R. and the variation with mixture strength, when ignition is by compression, is described in some detail in the text and illustrated by numerous graphs. The graphs for the relation between Opt. C.R. and mixture strength were always of the W form similar to those given in Part XIX for acetaldehyde and diethyl ether, obtained in like special conditions. The graphs indicate, as explained in Part XX, that the departure of thermal efficiencies from ideal values may be attributed in part to the adverse effect of the endothermic decomposition reaction required to provide nuclei of ignition during the compression stroke. Pressure–time indicator diagrams for an extremely weak heptane–air mixture are given. They show that maximum combustion pressure occurs at 10° after t.d.c. when compression ratio is adjusted for maximum power output, that is to the optimum value. Also that maximum combustion pressure timing advances as compression ratio is raised beyond the optimum value until it occurs before t.d.c. and power output becomes zero. The preignition thus obtained with compression ignition is described as nuclear preignition. The pressure–time diagrams show two stages of combustion

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Contribution from Defence Research Board, Ottawa, Canada, in association with the Department of Mechanical Engineering, University of Toronto, Toronto, Ont.

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very clearly. The first stage is regarded as including the delay period in part. The two stages are shown in a striking manner by a dp/dt diagram. A pressure–time diagram taken at nearly correct mixture shows that maximum combustion pressure at Opt. C.R. occurs as before at 10° after t.d.c. but that combustion is a single stage effect with pressure rising extremely rapidly. The experimental results mentioned above were all obtained with blank steel plugs in place of the spark plugs and bouncing pin. It was found however, on replacing one of the blank plugs with an unfired spark plug, that optimum compression ratios corresponding to mixtures richer than approximately 30% weak were substantially reduced. The igniting effect remained after removal of the electrodes. It could not be due to direct surface ignition in the low temperature conditions of the experiments and is attributed to the initiation of a pressure wave by the preferential decomposition and consequent nuclear ignition of the mixture adjacent to the spark plug core which is probably the surface of maximum temperature in the combustion chamber. It was found earlier that spark ignition at 10° in advance of t.d.c. became ineffective for mixtures leaner than approximately 40% weak. A similar spark ignition failure was shown by experiments of this Part made with spark timing varied from 20° to 5° advance. Compression ratio was always adjusted to the optimum value in order that maximum combustion pressure would occur at 10° after t.d.c. The Opt. C.R. attained relatively high values as spark ignition was retarded and the graphs relating it to mixture strength tended to assume the W form obtained with ignition by compression indicating that at relatively high values of Opt. C.R. impregnation of the mixtures by products of fuel decomposition was sufficient to increase rate of flame propagation but not to cause autoignition. As spark ignition became ineffective it was succeeded by compression ignition provided compression ratio were always raised to at least the optimum value as mixture strength was reduced. Special experiments for which power was supplied to maintain speed when B.H.P. became less than zero demonstrated that ignition by compression occurred even when the mixture was leaner than 93% weak, that is when the air–fuel ratio by weight was greater than 220:1. Systematic examinations of the deposits remaining on surfaces in the combustion chamber were made in the course of the compression ignition experiments described in this Part. The first indication of a deposit was a brown color found on the cooler surfaces after the briefest possible time of running. It could be wiped off easily and it is of interest that a similar color was found on surfaces in the combustion space of the M.I.T. machine after an ignition by compression of a hydrocarbon fuel. The color was therefore not due to decomposition of lubricating oil. In the engine, the color became a definite deposit of a granular nature after some hours of running on a weak mixture and appeared to be of a resinous nature which indicated condensation products of aldehyde. Some carbon was however generally present. Finely divided carbon appeared as the sole deposit as mixture strength was increased until at correct mixture the carbon deposit covered a large part of the combustion chamber surface. At richer mixtures the carbon formed a layer over the entire surface and black smoke appeared in the exhaust. The ignition characteristics exhibited by the experiments described in this Part and earlier in Part XIX are obtainable solely in conditions of low heat load which ensures that decomposition and oxidation reactions occur mainly if not entirely in the gaseous phase. Thus it is shown by the final experiments of this Part that when heat load is increased by raising the jacket coolant and mixture temperatures to the values used for the motor method of knock rating, other conditions of the method of experiment remaining unchanged, the relation between Opt. C.R. and mixture strength tends to be represented by a single graph regardless of whether ignition is by compression with or without an unfired spark plug or by spark at 10° in advance of t.d.c. and a transition occurs from the W to the familiar U form of graph.

INTRODUCTION

Experiments described in Part XVII (4) demonstrated that a standard C.F.R. knock testing engine could be run without spark ignition over a wide range of pentane–air mixtures if compression ratio were always adjusted to maintain a particular standard of knock intensity as indicated by the bouncing pin meter. Volumetric efficiency and consequent charge density were higher than usual because the shrouded inlet valve had been replaced with one of the common type,

the engine was run at the low speed of 400 r.p.m. and the air supply and jacket coolant maintained at unusually low temperatures. Exceptionally high values were obtained for thermal efficiency although compression ratio could not be increased sufficiently, when using other than weak mixtures to obtain a value corresponding to maximum power output, because of the incidence of a knock intensity greater than that adopted as standard.

It seemed remarkable at the time that a carburetor type engine in exceptionally cool conditions of operation would run without spark ignition because that effect in practice generally occurs when an engine is hot and is then attributed to preignition arising from a surface in the combustion chamber, such as a spark plug or an exhaust valve, having become overheated. It was concluded from a consideration of the characteristics of performance of the engine that ignition had been by compression and a consequence of the decomposition of the fuel to provide nuclear centers of ignition in the combustible mixture.

The method of experiment was next used for a determination of the combustion characteristics of acetaldehyde and diethyl ether although both substances knock violently when used as engine fuels in normal operating conditions. The experiments are described in Part XVIII (5). The results demonstrated that the combustion characteristics, in the low engine temperature conditions, were broadly similar to those previously obtained when using pentane. Thus although compression ratio could be adjusted until the engine would run without spark ignition, it could not be increased further to obtain maximum power output unless the knock intensity adopted as standard were exceeded. Moreover, the audibility of knocking combustion did not always correspond with the intensity indicated by the knock meter. Furthermore, in view of the ease of vaporization by ether and acetaldehyde it appeared that the presence of liquid drops in the fuel–air mixture was not essential to the decomposition of the fuel to the extent necessary for the provision of nuclear centers of ignition.

Subsequent to the experiments mentioned above it was found that if charge density were below normal, compression ratio could be raised and adjusted to the value required for maximum power output without giving rise to an excessive intensity of knocking combustion even when using correct mixtures with air of either acetaldehyde or diethyl ether. This procedure made possible a determination of the relation between compression ratio and maximum power output for any value of mixture strength. Experimental results obtained accordingly were more easily repeatable and more significant than those obtained by adjusting compression ratio for a standard knock intensity as indicated either by the bouncing pin or by the level of audibility.

Refrigeration equipment for the air supply to the carburetor was provided at this stage of the investigation, and it was no longer necessary to rely upon uncertain winter weather for a supply of dry cold air. Thus the conditions required for what had developed into a new method of experiment could be standardized in order that comparable results might be obtained for experiments with various fuels when ignition was either by spark or compression.

The conditions adopted as standard, and the arrangements made to provide them, are described in some detail in Part XIX (6). Those of prime importance are stated here as a convenience and are: (1) a subnormal charge density; (2) an engine speed of 400 r.p.m.; (3) jacket coolant at 95°F. inlet, 100°F. outlet; (4) air supply to carburetor 50°F.; (5) spark ignition when used, 10° in advance of arrival of the piston at top dead center (t.d.c.); and (6) compression ratio always adjusted to obtain maximum power output, that is, to an optimum value.

The new method of experiment was used for the experiments with acetaldehyde and diethyl ether described in Part XIX (6) and for those with methanol, for which spark ignition was necessary, described in Part XX (3). The experimental results appeared to be of considerable interest in respect of the nuclear theory of ignition and the fundamentals of detonation but because of recent publication they need not be discussed here. It should be mentioned, however, that the carburetor type engine seemed to have become a compression ignition machine comparable in many respects with the single stroke variety while possessing the advantage that characteristics of compression ignition could be related to engine performance in terms of power and thermal efficiency. It was decided, therefore, to use the new method of experiment for a further investigation of the combustion characteristics of *n*-pentane and in addition for a determination of those of hexane and heptane.

Normal paraffins as supplied by Phillips Petroleum Company were used for the experiments. The pentane and hexane were technical grades. The heptane was the nearly normal grade approved by the A.S.T.M. as a reference fuel for knock rating. Relevant data are tabulated below.

The lower calorific values of Table I were used for calculating thermal efficiencies.

TABLE I

DATA IN RESPECT OF THE PARAFFIN FUELS

	Pentane	Hexane	Heptane
Boiling point, normal variety, °F.	96·9	155·7	209·2
Heat of vaporization, B.T.U./lb. at b.p.	153·6	144·8	137·5
Higher calorific value, B.T.U./lb.	20914	20771	20668
Lower calorific value, B.T.U./lb.	19345	19238	19160
Correct A/F ratio, by weight	15·31	15·24	15·18

A C.F.R.-F.2 engine with a swinging field d-c. electric dynamometer was used and differed from standard in being fitted with three spark plugs and an unshrouded inlet valve.

The volumetric efficiency in the standard conditions of the new method of experiment was 85%. The corresponding charge density is described as "normal". Charge densities of 64 and 78% of normal were used in the course of the experiments. If pressure at the beginning of compression were atmospheric, volumetric efficiency at a particular temperature would be 100% and

the charge densities of 64 and 78% at the same temperature would be approximately 54 and 66% of atmospheric density.

The terms compression ratio, optimum compression ratio, and mixture strength are abbreviated in the text to C.R., Opt. C.R., and M.S., respectively.

RESULTS OF EXPERIMENTS

Compression Ignition and the Determination of Optimum Compression Ratio

The method adopted for the determination of optimum compression ratio, when ignition is by *compression*, cannot be used with fuels liable to detonation unless charge density is less than normal, as shown by the experiments with acetaldehyde and diethyl ether described in Part XIX (6). The application of the method to more comprehensive experiments with paraffin fuels requires an elaboration of its earlier description and experiments made with hexane and heptane will suffice for the purpose. The experiments were made with a charge density of 64% of normal after substituting blind plugs of mild steel for the three spark plugs and the bouncing pin.

The engine was started from cold with little or no shock by using a relatively high compression ratio and a weak mixture. This starting method was used for a series of experiments extending over a period of several weeks during which spark ignition was never used. After starting in this way, C.R. was reduced and the engine run for the time required to stabilize temperatures. The rate of fuel consumption and the power output (B.H.P.) were then observed; speed being maintained at 400 r.p.m. by manual control. The operation was repeated as C.R. was varied by steps, in order to obtain values of power output passing through a maximum. The results were then plotted to obtain a graph for the relation between power output and C.R. for the particular value of the M.S. A similar relation between power output and C.R. was then obtained for other values of M.S. and a series of graphs plotted accordingly.

A selection from the series obtained as a result of experiments with hexane is exhibited by Fig. 1, and it will be seen that for any one of the values of M.S. there is a particular C.R. for which power output is a maximum. The broken line graph drawn through the optimum values thus determined is of the W form similar to that given in Part XIX (6) as a result of experiments with acetaldehyde and diethyl ether, but the form is distorted because of the non-linear relation between power and M.S. All of the graphs required to delineate the broken line graph are not shown because of the complexity that would be due to overlapping. A similar set of graphs but plotted on a base of indicated mean effective pressure (I.M.E.P.) is given, Fig. 2, for experiments with heptane.

A comparison of Figs. 1 and 2 shows that, for medium rich mixtures, the graphs relating C.R. and I.M.E.P. (Fig. 2) do not exhibit the well-defined Opt. C.R. shown when C.R. was related to B.H.P., as in the graphs of Fig. 1. The comparison shows also that the knock intensity for rich hexane–air mixtures, as described, is heavier than for similar heptane–air mixtures. The

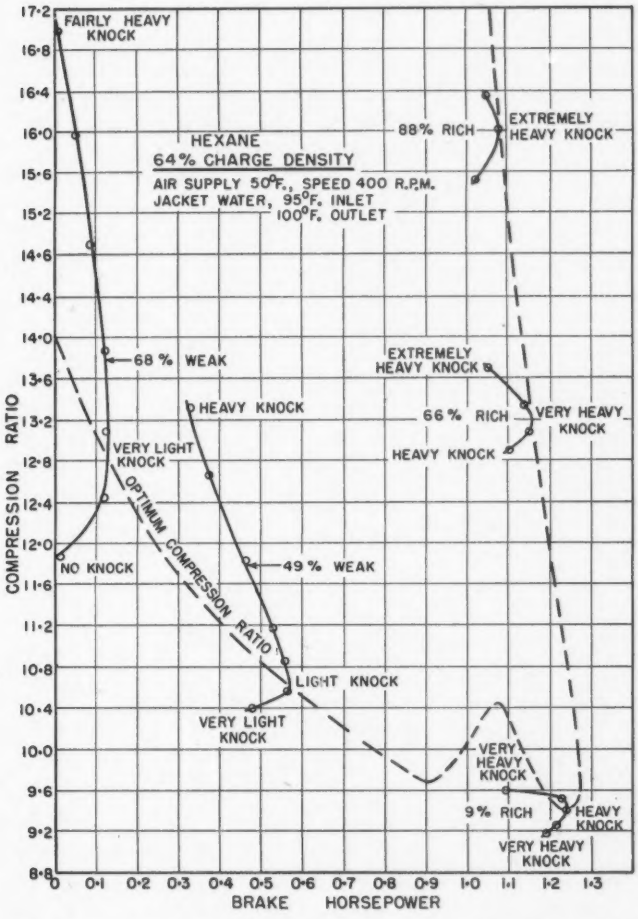


FIG. 1. Results of experiments made to determine optimum compression ignition timing. Hexane–air mixtures.

difference is attributed to the higher compression ratios required for the nuclear ignition of hexane. Thus further experiments described in this Part, see Fig. 6, show that for a hexane–air mixture 80% rich the Opt. C.R. was 16 whereas an Opt. C.R. of 12.5 only was required with a similar concentration of heptane in the mixture with air.

Nuclear Preignition

It has been assumed that ignition by compression is a nuclear effect and Opt. C.R. has been taken as the value for which power output (B.H.P.) was a maximum. The time of the occurrence of maximum combustion pressure, in

degrees of crank angle after t.d.c. must then have been the optimum. The decrease of power output observed as compression ratio is *raised* to beyond the optimum value, when using a particular value of mixture strength, is therefore attributed to the corresponding advance in the time of occurrence of maximum combustion pressure. That time is dependent on the time of nuclear ignition and the length of the delay period, and the decrease of power output is attributed to nuclear preignition. On the other hand, the decrease of power observed as C.R. is *lowered* from the optimum value is attributed to a retardation of the time of occurrence of maximum combustion pressure and the corresponding time of nuclear ignition. Thus, referring to Fig. 2, it will be seen that for heptane–air mixtures, 71, 62, and 53% weak, C.R. could be raised beyond the optimum value until power output became zero, without the occurrence of an intolerable knock intensity.

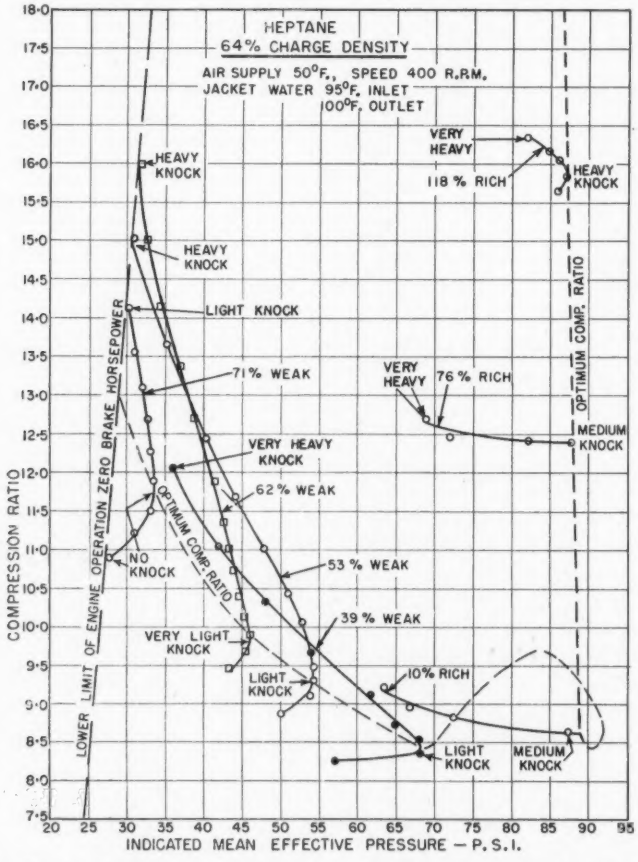


FIG. 2. Results of experiments made to determine optimum compression ignition timing. Heptane–air mixtures.

The possible *decrease* below the optimum value was relatively small. That is, there was a narrow variation of C.R. between the optimum and the value for which ignition did not occur or for which B.H.P. was zero.

Data from Fig. 2, relating to the effect of nuclear preignition obtained on using compression ratios higher than the optimum value, are tabulated below for heptane–air mixtures ranging from 39% weak to 118% rich. These are mixtures for which C.R. could not be raised sufficiently to reduce power output to zero because of the consequent intolerable intensity of knocking combustion.

What is described in the table as "very heavy knock", which was always accompanied by unstable running, may be taken as indicating the maximum permissible degree of nuclear preignition, that is, ignition occurring at a higher than the Opt. C.R. Then, on this basis, the engine will, for example, tolerate a degree of nuclear preignition sufficient to reduce indicated power by 45% when the mixture is 39% weak, by 29% when it is 10% rich, and by 6% only when it is excessively rich.

It is to be remembered that the data of Table II were obtained in the standard conditions of the new method of experiment and when the charge density was 64% of normal.

TABLE II

DECREASE OF POWER WITH INCREASE OF COMPRESSION RATIO TO BE HIGHER THAN THE OPTIMUM VALUE

Mixture strength	C.R. for max. power	C.R. for v. heavy knock	I.M.E.P. decrease	Per cent decrease
39% weak	8·4	12·1	From 68 to 36	47
20% "	9·4	10·7	" 84 to 53	37
10% rich	8·6	9·2	" 89 to 63	29
72% "	12·4	12·7	" 87 to 69	21
118% "	15·8	16·4	" 87 to 82	6

Characteristics of Nuclear Preignition, Two Stage Combustion, and the Delay Period as Shown by Indicator Diagrams

A Sunbury electronic indicator with a variable magnetic flux pressure pickup was used to obtain the diagrams. A notched timing wheel mounted on the outboard end of the dynamometer shaft of the C.F.R.-F.2 unit, provided blips on pressure–time diagrams at 10° intervals. The lack of uniform spacing of the blips as they appear on the diagrams is due to the variable pressure on the engine piston acting on a somewhat flexible transmission to the timing wheel. The blips on the pressure–time diagrams as reproduced have, for the sake of clarity, been indicated by added vertical lines. Long vertical lines indicate blips at t.d.c. and shorter ones, those at 10° intervals for 30° before and after t.d.c.

The diagrams, Figs. 3, 4, and 5, were taken when the engine was running on compression ignition in the standard conditions of the new method of experiment, with charge density 64% of normal. They depict the characteristics of combustion as described below. The term "maximum combustion pressure" will be abbreviated to Max. C.P. because of frequent use.

Referring to diagram No. 1 of Fig. 3, it will be seen that Max. C.P. is at 18° after t.d.c. with a C.R. of approximately 10.

Diagram No. 2 shows that an increase of C.R. to 10.3 caused Max. C.P. to advance 8°, that is, to 10° after t.d.c., and the graph relating C.R. to power shows that I.M.E.P. had increased from 30 to 32.5 p.s.i. which is the maximum attained. The C.R. of 10.3 may therefore be taken as the optimum value.

Diagram No. 3 shows the effects of raising the compression ratio to 10.9. The Max. C.P. increases but as C.R. is then higher than the optimum value, I.M.E.P. decreases from the maximum of 32.5 to 31.0 p.s.i. This effect is due to the advance of Max. C.P. from 10° to 6° after t.d.c. and the consequent beginning of nuclear preignition.

Diagram No. 4 shows the effects of a further increase of C.R. to 12.8. Max. C.P. advances to 4° before t.d.c. and rises to a relatively high value but, as it occurs before t.d.c., I.M.E.P. is reduced to 29 p.s.i. which is the value obtained when B.H.P. is zero. That is, an advance in the time of occurrence of Max. C.P., of from 10° after, to 4° before, t.d.c., has had the effect of reducing power output from the maximum possible value to zero because of the degree of nuclear preignition.

The diagrams of Fig. 3 show two stages of combustion. The first is regarded as the "delay period" and diagram No. 1 shows that it extends from 10° before to 10° after t.d.c. when C.R. is 10.0. Therefore the phenomenon occurs at nearly constant volume but with a pressure rise during the 10° before t.d.c. The time of the occurrence of the delay period advances as C.R. is increased and the length in degrees of crank angle diminishes until, with a C.R. of 12.8 it begins at 13° and ends at 9° before t.d.c. Thus at the engine speed of 400 r.p.m., the time of the delay period diminishes from 8.4×10^{-3} sec. to 1.7×10^{-3} sec. as the C.R. is raised from 10 to 12.8.

It will be seen by further reference to the diagrams of Fig. 3 that the fillet connecting the two stages of combustion pressure rise tends to disappear as C.R. is raised. It is well rounded at a C.R. of 10 and extends over 10° of crank angle which is the time taken by the second combustion pressure rise. The fillet scarcely exists at a C.R. of 12.8, diagram No. 4, and the time taken by the second pressure rise is then not greater than 4° of crank angle or 1.7×10^{-3} sec.

The diagram, Fig. 4, for rate of change of pressure with time, dp/dt, is complementary to diagram No. 2 of Fig. 3, and should be compared with it. Thus during compression, rate of change is nearly constant for approximately 12° of crank angle before the first combustion pressure rise which begins at 8° before t.d.c. The rate then increases but falls to zero at the end of the first period of combustion and the beginning of the second combustion pressure rise. It then rises to a maximum and falls to zero as the combustion pressure reaches a maximum at 10° after t.d.c. and expansion begins. Rate of change then increases again but with a negative value, rapidly at first and then relatively slowly until expansion is complete and rate of change becomes zero.

Indicator diagrams taken for relatively rich mixtures do not show a marked first pressure rise. The diagram of Fig. 5, taken at the Opt. C.R. of 10 when

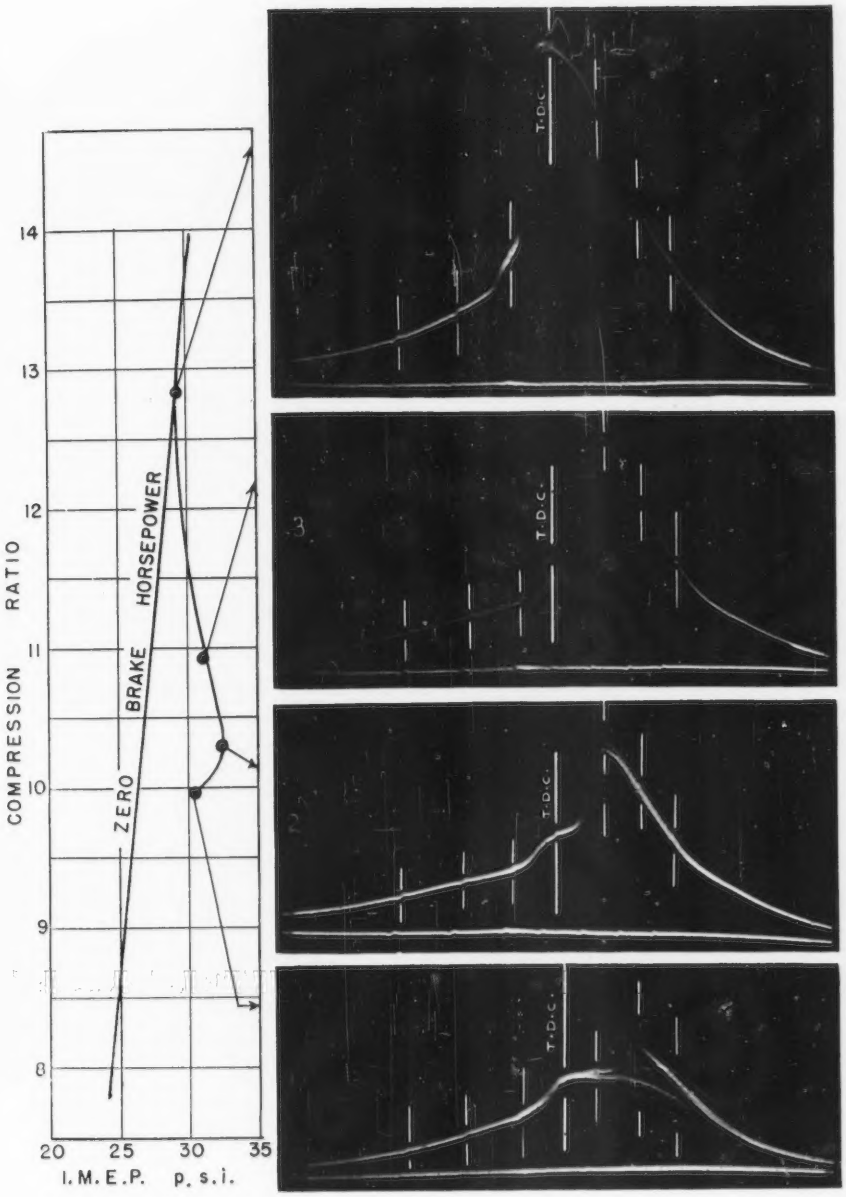
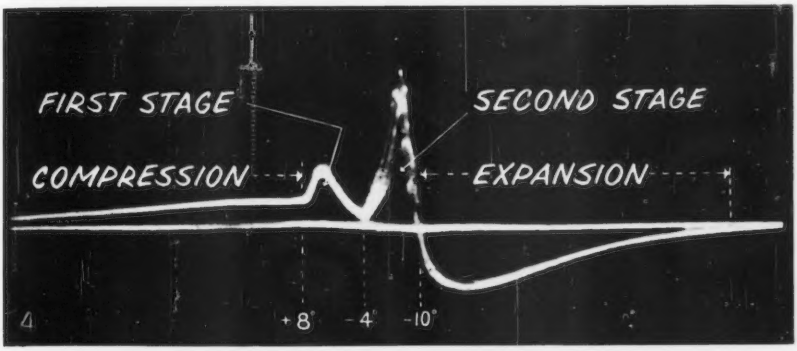


FIG. 3. Pressure–time indicator diagrams, showing two stage ignition, the advance in timing of maximum combustion pressure as C.R. is increased and the occurrence of maximum power output when combustion pressure is a maximum at 10° after t.d.c. Heptane–air mixture 70% weak, ignition by compression with blind plugs.



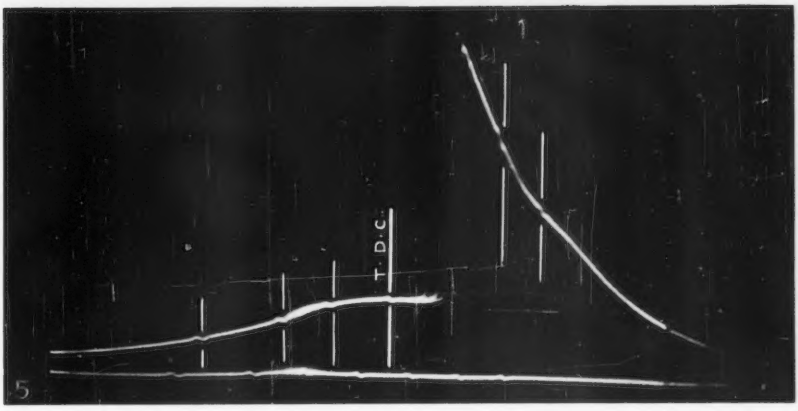


FIG. 4. Rate of change (dp/dt) indicator diagram taken at Opt. C.R. and showing first stage of ignition, beginning at 8° before and ending at 4° after t.d.c., with maximum combustion pressure occurring 10° after t.d.c. Heptane–air mixture 70% weak, ignition by compression with blind plugs.

FIG. 5. Pressure–time indicator diagram taken at Opt. C.R. with a nearly correct heptane–air mixture and showing a single stage ignition with maximum combustion pressure occurring at 10° after t.d.c. Ignition by compression with blind plugs.

using a nearly correct pentane–air mixture shows only a slight first pressure rise between 20 and 10° before t.d.c. Thus the pressure time line is nearly horizontal from 10° before t.d.c. to the beginning, at from 6 to 9° after t.d.c., of the extremely rapid combustion pressure rise. It will be noted that the diagram includes three cycles which do not repeat exactly in respect of the time of occurrence of the combustion pressure rise.

The Relation Between Opt. C.R. and M.S. With Ignition by Compression and the Effect of Charge Density

It is apparent from the experimental results exhibited by Figs. 1 and 2 that a graph drawn through the Opt. values of C.R. would be of a W form similar to that obtained when using acetaldehyde and diethyl ether as engine fuels in the standard conditions of the new method of experiment (6). The broken line graphs of Figs. 1 and 2 drawn accordingly are necessarily of a distorted W form because they are plotted on a base of power developed and the relation between power and M.S. is not linear as mentioned earlier.

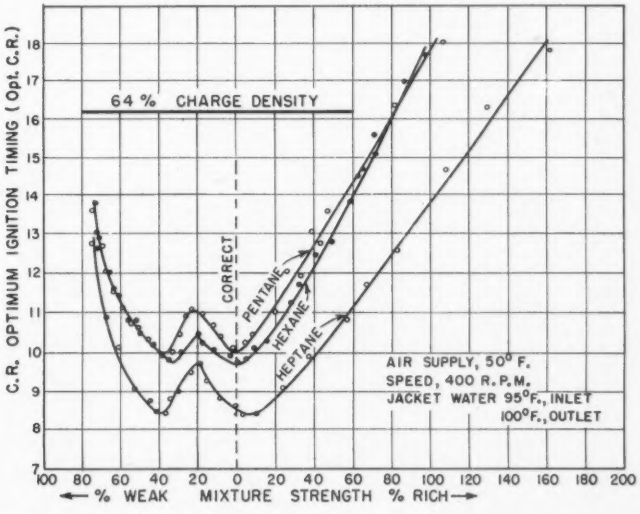


FIG. 6. Relation between Opt. C.R. and mixture strength at 64% of normal charg density. Experiments with heptane, hexane, and pentane. Ignition without spark plugs.

The experiments presently to be described were made in the conditions used for those with acetaldehyde and diethyl ether and similarly with blind steel plugs replacing the spark plugs and bouncing pin. Pentane, hexane, and heptane were used as fuels at two charge densities, namely, 64 and 78% of normal and with values of M.S. ranging from 76% weak to over 100% rich. The C.R. was adjusted for maximum power at every M.S. used. The experimental results obtained at 64% of normal charge density are exhibited by the graphs of Fig. 6; those obtained at 78% by the graphs of Fig. 7. The graphs are plotted on a

M.S. base and are always of a nearly symmetrical W form, with two minimum values of Opt. C.R. and an intermediate maximum. A minimum occurs for mixtures 40% weak and again for the correct mixture. The intermediate maximum occurs for mixtures 20% weak. The percentages as applied to the three fuels and the two charge densities are approximate. The W form is most pronounced for the heptane–air mixtures for which both minimum values of Opt. C.R. were 8.4 at 64% of normal charge density, Fig. 6, and 8.1 at 78%, Fig. 7. The minimum values of Opt. C.R. for pentane were equal at 10, at the lower charge density, but at the higher, Opt. C.R. for the first minimum was 9.7 and 9.5 for the second. These small differences and similar ones observed when using hexane at differing charge densities are probably within the accuracy of measurement because they have been found to vary with the degree of piston and cylinder wear, the surface condition of the combustion chamber and the time taken between changes of M.S. for the stabilization of surface temperatures in the combustion chamber.

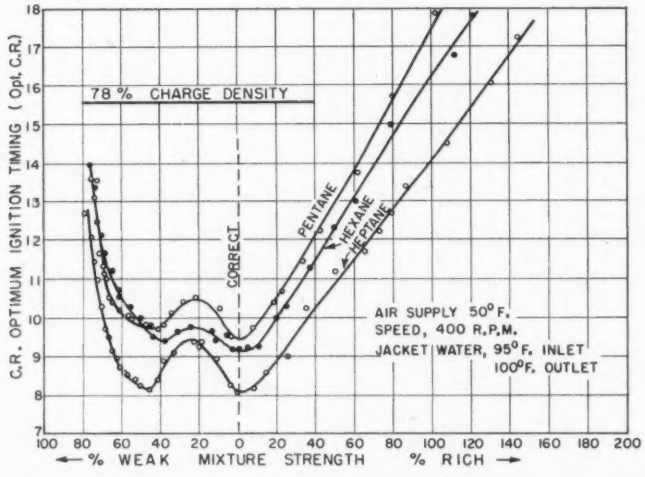


FIG. 7. Relation between Opt. C.R. and mixture strength at 78% of normal charge density. Experiments with heptane, hexane, and pentane. Ignition without spark plugs.

The effects of increasing charge density from 64 to 78% of normal were, as is shown by a comparison of the graphs of Figs. 6 and 7 to lower the values of Opt. C.R. over the entire range of M.S., except in the case of rich heptane–air mixtures, and to move the minimum and maximum values of Opt. C.R. slightly to weaker mixtures. Knock intensity for particular values of M.S. increased on increasing charge density. The small differences due to the relatively small change of charge density were difficult to measure accurately for the reasons mentioned above.

Power and Thermal Efficiency With Compression Ignition and Optimum Compression Ratio

Relevant data are available from the results of the experiments with pentane, hexane, and heptane made at two charge densities. The results of the six sets of experiments are, however, similar in character and it will suffice for the present to describe those obtained when using pentane at 64% of normal charge density with M.S. ranging from 74% weak to 107% rich. Data for indicated and brake horsepower are given by the graphs of Fig. 8 and for indicated and brake thermal efficiencies by those of Fig. 9. A graph for the relation between Opt. C.R. and M.S. is given on both figures for convenience of reference.

The results exhibited by the graphs of Fig. 8, show that while maintaining optimum nuclear ignition timing, it was possible to reduce M.S. until brake horsepower became zero. Maximum power, both indicated and brake, was obtained with the correct mixtures and on increasing M.S. to be 107% rich, indicated power diminished by 6% only from the maximum. A greater percentage decrease of brake power occurred because friction loss increased from 0.54 to 0.65 horsepower on increasing the C.R. from 10 to 18.

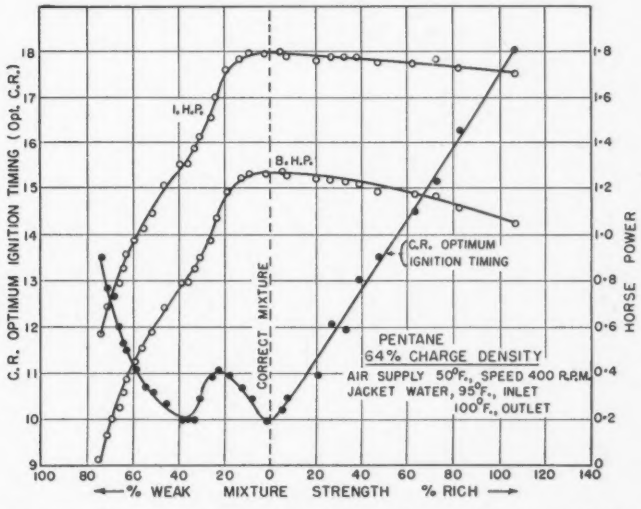


FIG. 8. Indicated and brake horse power at Opt. C.R. and 64% of normal charge density for pentane–air mixtures ranging from 75% weak to 105% rich. Ignition without spark plugs.

The results exhibited by the graphs of Fig. 9 show that indicated thermal efficiency attained a maximum of 41% for a mixture 60% weak used at an Opt. C.R. of 17. A maximum of 25% was obtained for brake thermal efficiency when the mixture was 20% weak at an Opt. C.R. of 11. The thermal efficiencies are regarded as high values in view of the relatively low charge density and the correspondingly large proportion of the heat of combustion lost to the cool

surfaces of the combustion chamber which has relatively large surface to volume ratios at the high values of C.R. required for optimum compression ignition timing. It is difficult when using the extremely weak mixtures required for maximum thermal efficiency, and with brake horsepower approaching zero, to maintain experimental conditions sufficiently steady for a high degree of accuracy of measurement. Thus it will be noted that the experimental points for indicated thermal efficiency do not all lie on the graph. The irregularity is attributed to inaccurate measurement of the horsepower absorbed by mechanical and fluid friction which is added to the observed brake horsepower to obtain the indicated value. Thus it will be seen that values for brake horsepower, Fig. 8, obtained by direct measurement, fall well on the corresponding graph.

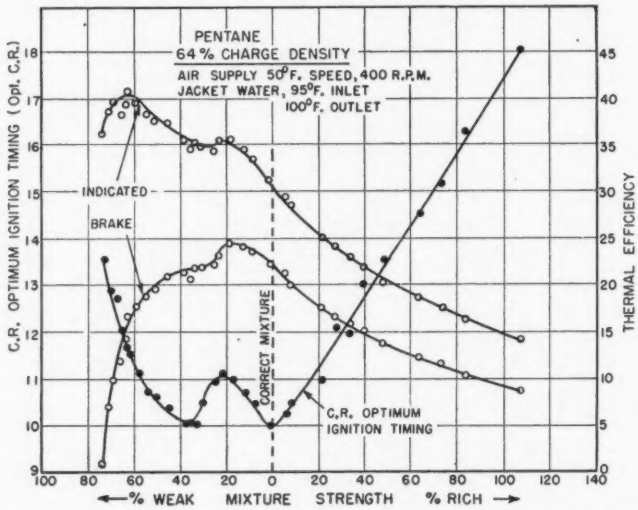


FIG. 9. Indicated and brake thermal efficiency at Opt. C.R. and 64% of normal charge density for pentane–air mixtures ranging from 75% weak to 105% rich. Ignition without spark plugs.

The Initiation of Nuclear Ignition by an Unfired Spark Plug

The ignition of the fuel–air mixture by compression after blind plugs had replaced the spark plugs and bouncing pin occurred only at relatively high compression ratios and was attributed, in Part XIX (6), to ignition being then made possible by decomposition of the fuel during compression to yield nuclear centers of ignition. Furthermore, it was suggested in Part XX (3) that nuclear ignition of the entire charge, instead of the end gas only, could be due to a pressure wave started by the preferential nuclear ignition of a small volume of mixture adjacent to an overheated surface such as an exhaust valve. It may safely be assumed that the exhaust valve was the hottest surface in the combustion chamber when no spark plugs were used and that a still hotter surface was

provided on the replacement of a blind steel plug by the ceramic core of an unfired spark plug. It therefore became of interest to determine the characteristics of nuclear ignition when one of the blind plugs was replaced by an unfired spark plug.

The ceramic core of most types of spark plug is known to attain a higher temperature than the exhaust valve, and the plug used for the experiments was Champion No. 8, which is specified for use with the C.F.R. knock testing engine. The length of the exposed part of the ceramic core is $\frac{7}{8}$ in. The plug was always used in the standard position in the wall of the combustion chamber, midway between the exhaust and inlet valves and diametrically opposite the bouncing pin position.

Heptane was used for the first series of experiments, made when using mixtures ranging from 60% weak to 30% rich, with the object of determining corresponding values of Opt. C.R., with no spark plug, with one unfired spark plug, and with the spark plug fired at 10° in advance of t.d.c. Charge density was 78% of normal. The experimental results are exhibited by the graphs of Fig. 10.

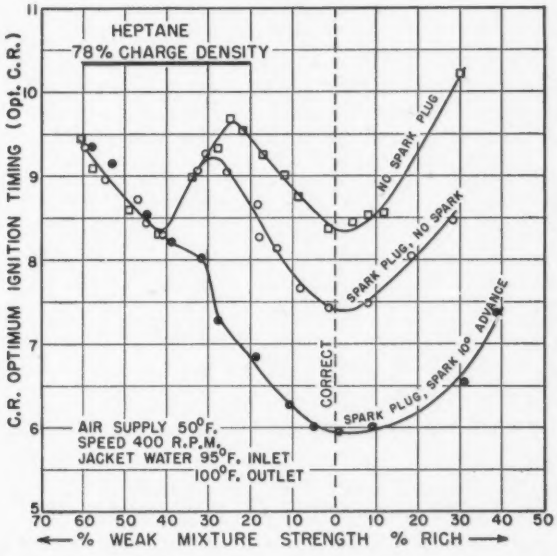

HEPTANE
78% CHARGE DENSITY
C.R. OPTIMUM IGNITION TIMING (Opt. C.R.)
NO SPARK PLUG
SPARK PLUG, NO SPARK
CORRECT
SPARK PLUG, SPARK 10° ADVANCE
AIR SUPPLY 50°F.
SPEED 400 R.P.M.
JACKET WATER 95°F. INLET
100°F. OUTLET
70 60 50 40 30 20 10 0 10 20 30 40 50
% WEAK MIXTURE STRENGTH % RICH

FIG. 10. Relation between Opt. C.R. and mixture strength with ignition by compression without spark plugs, with one unfired plug, and by a plug fired at 10° before t.d.c. Heptane–air mixtures, 78% of normal charge density.

The upper graph of the figure is for results obtained when the spark plugs and bouncing pin were replaced with mild steel blind plugs. The combustion chamber surface of maximum temperature was then that of the exhaust valve and the graph showing the relation between Opt. C.R. and M.S. is of the W form as described earlier and is similar to that obtained in similar conditions

when acetaldehyde and diethyl ether were used as engine fuels, Part XIX (6). There are two minimum values of 8.4 for Opt. C.R., one for a mixture 40% weak and another for the correct mixture. The intermediate maximum value is 9.7 for a mixture 25% weak.

The middle graph of the figure is for results obtained when an unfired spark plug in the standard position replaced a blind plug. It is evident from a comparison of the upper and middle graphs that the unfired plug possessed an igniting effect which became apparent with mixtures richer than 30% weak. Thus when the M.S. was increased to be correct, the corresponding Opt. C.R. was 8.4 with no spark plug and 7.4 with an unfired plug. The igniting effect of the unfired plug continued to increase with increase of M.S. and for a mixture 30% rich, reduced the value of the corresponding Opt. C.R. from 10.2 to 8.6.

The results obtained when the spark plug was fired 10° in advance of t.d.c. are shown by the lower graph of Fig. 10. It is of the conventional U shape over the range of mixture strength for which spark ignition was effective, with Opt. C.R. for the correct mixture having the relatively low value of 5.9.

The igniting effect of an unfired spark plug was again demonstrated by a series of experiments with pentane made in the conditions similar to those used for heptane but over a wider range of mixture strength, extending from 75% weak to over 100% rich. The results are given by the two sets of graphs of Fig. 11. The upper set is for the relation between indicated thermal efficiency and M.S.; the lower is for the relation between Opt. C.R. and M.S

It will be seen by reference to the lower set of graphs that the characteristics of nuclear ignition at Opt. C.R., with and without an unfired spark plug, are similar to those determined for heptane–air mixtures as shown by the graphs of Fig. 10, but values of Opt. C.R. are approximately 1.5 ratios higher. It was mentioned when describing the similar experiments with heptane that the igniting effect of the unfired plug increased as M.S. was increased to be 30% rich. A similar effect was obtained with pentane as shown by the graphs of Fig. 11, but it will be noted that the igniting effect tended to diminish as the M.S. was further increased to be 100% rich.

The lower graph of Fig. 11 which exhibits the results obtained when the spark plug was fired is, as for the similar experiments with heptane, of symmetrical U shape over the greater part of the range of mixture strength for which spark ignition is effective. It is, however, a narrower U and displaced toward relatively rich mixtures. Thus the minimum value of Opt. C.R. for pentane was 6.0 for a mixture 10% rich while that for heptane was 5.9 for a correct mixture, but for mixtures 30% weak, Opt. C.R. for pentane was 1.5 ratios higher than for heptane.

It is of interest that the three graphs of Fig. 11, for the relation between Opt. C.R. and M.S. tend to coincide only as the mixture becomes extremely rich while the graphs for related *indicated thermal efficiencies* do coincide for mixtures more than 40% rich, although Opt. C.R. is then 7.1 with spark ignition, 10.1 with the spark plug unfired, and 12.7 with no spark plug. On the other hand,

the graphs for thermal efficiencies do not coincide over the mixture range 40 to 60% weak although the related values of Opt. C.R. are identical within the accuracy of experiment. There is, however, an apparent tendency for the values of thermal efficiency to coincide for mixtures leaner than 60% weak.

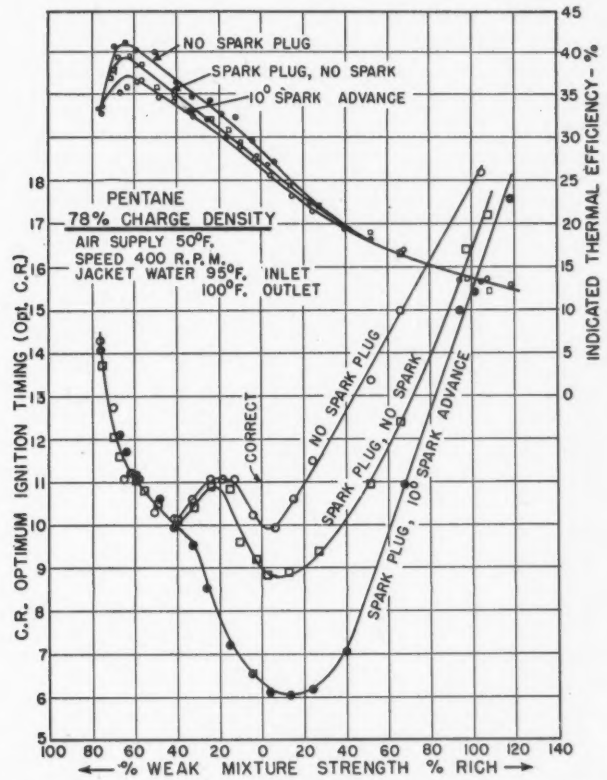


FIG. 11. Relation between Opt. C.R. and mixture strength with ignition by compression without spark plugs, with one unfired plug, and by a plug fired at 10° before t.d.c. Also graphs for corresponding values of indicated thermal efficiency. Pentane–air mixtures, 78% of normal charge density.

The Transition From Spark to Compression Ignition

A transition from ignition by spark to ignition by compression as M.S. is reduced and C.R. increased to maintain an optimum value has been found by experiments already described, to occur solely when using fuels which in the corresponding temperature and pressure conditions decompose thermally to form material nuclei of ignition. The transition has always occurred within the M.S. range 40 to 50% weak when spark ignition timing was fixed at 10° in advance of t.d.c. The particular spark ignition timing was chosen merely as a

reasonable value for early experiments with acetaldehyde and was retained for comparable experiments with other liquid fuels. It therefore became of interest to determine whether the transition always occurred within the same range of M.S. when spark ignition timing was set later or earlier than 10° advance and whether a spark timing other than 10° in advance of t.d.c. should have been used.

The results of four sets of experiments made accordingly when using spark settings of 20, 15, 10, and 5° in advance of t.d.c. are given by the graphs of Fig. 12. Heptane was used as the fuel with charge density 78% of normal. Broken line graphs for compression ignition with the spark plugs replaced by blind plugs and with one plug unfired, as reproduced from Fig. 10, have been added to the figure.

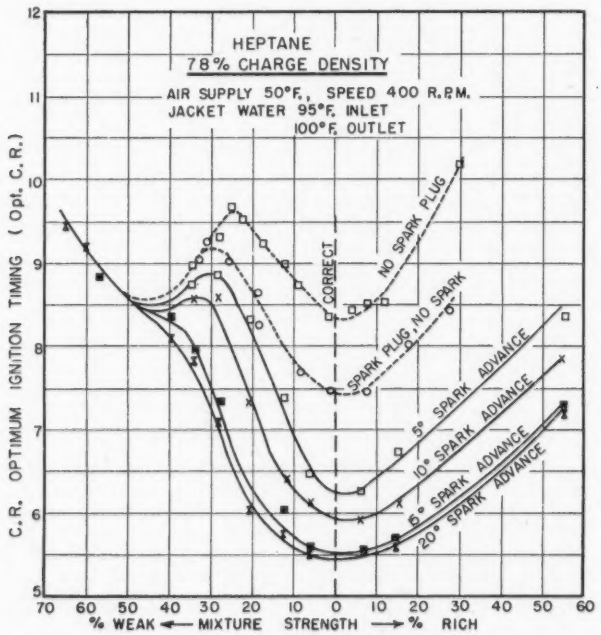


FIG. 12. Relation between Opt. C.R. and mixture strength with spark ignition at 5 to 20° before t.d.c. Heptane–air mixtures, 78% of normal charge density.

The graphs of the figure show that the relation between Opt. C.R. and M.S. tends rapidly to become unaffected by spark timing as M.S. is reduced to be leaner than 40% weak until with a mixture 48% weak the effect of spark timing is nil. Then as M.S. is further reduced ignition can be continued by the progressive increase of C.R. as required to maintain the optimum value.

The tendency of the graphs for spark ignition of mixtures leaner than 30% weak to assume the form of those for nuclear ignition, as spark timing is retarded, is of interest in respect of the nuclear theory. Thus when spark ignition is fixed

at only 5° in advance of t.d.c. and C.R. raised to *the optimum value*, combustion must be completed by approximately 10° after t.d.c., that is, 15° after the spark had passed. This is an impossibly brief interval in the usual circumstances of spark ignition. The probable explanation is that at the relatively high values of Opt. C.R. required for the effect, decomposition of the fuel had provided a concentration of nuclei sufficient for an exceptionally rapid propagation of the flame started by a spark but not sufficient for autoignition. It is difficult to obtain repeatable experimental results for the relation between Opt. C.R. and M.S. within the range of M.S. for which spark ignition is succeeded by compression ignition, even when the combustion chamber of the engine has been cleaned before beginning a set of experiments. The difficulty diminishes as spark timing is advanced but exists even with the 10° advance generally used for the experiments recently described. Thus referring to the preliminary experimental results of Fig. 10, it will be seen that the graph for 10° spark ignition advance exhibits an inflection only, over the mixture range 30 to 40% weak, whereas the similar graph, Fig. 12, obtained in like conditions and also with heptane, exhibits a definite reversal of direction.

The experimental results confirm that, irrespective of timing, spark ignition tends to become ineffective, in the conditions of the experiments, for mixtures leaner than 30 to 40% weak and completely so for those leaner than 50% weak. They show also that in the conditions of the experiments, the rate of change of Opt. C.R. with M.S., when spark ignition is used, is substantially independent of spark timing over a wide range of M.S. on both the weak and rich side of the correct value.

Compression Ignition as Affected by an Unfired Spark Plug With and Without Electrodes

Premature ignition in a carburetor engine running on spark ignition is frequently attributed to the electrodes of the spark plug having become incandescent. There was no evidence of that igniting effect having occurred in the temperature conditions of the experiments described in this and preceding parts, and it has been assumed accordingly that the ceramic core of the plug, not the electrodes, was responsible for the decrease of Opt. C.R. observed when a blind plug was replaced by an unfired spark plug, nevertheless, in order to remove any doubt, compression ignition experiments were carried out with an unaltered C.F.R. Champion No. 8 spark plug in the standard position and repeated immediately, after removal of the electrodes. Experiments were made with M.S. varied over the range for which significant results had been obtained when using an unfired spark plug as shown by the graphs of Figs. 10 to 12.

The experimental results are given by the graphs of Fig. 13. The broken line graphs are for results obtained with the unfired and unaltered spark plug set in the standard position. Experimental points are omitted in order to avoid confusion. The results obtained after removal of the electrodes are given by the marked experimental points. It is demonstrated accordingly that the igniting effect of an unfired spark plug as observed in the conditions of the compression ignition experiments of this Part is due to the ceramic core.

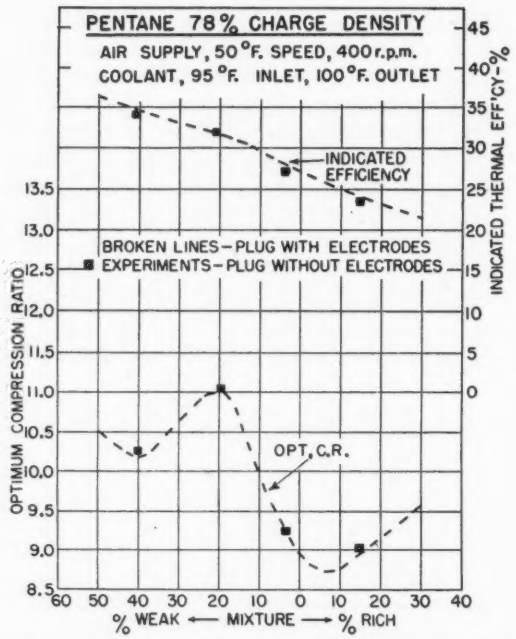


FIG. 13. Relation between Opt. C.R. and mixture strength and between Opt. C.R. mixture strength and indicated thermal efficiency, with an unfired spark plug with and without electrodes, in standard position. Pentane–air mixtures, 78% of normal charge density.

Maximum Combustion Pressures, Compression, and Spark Ignition

The maximum pressure attained in an engine cylinder can be measured by a Bourdon gauge, when a check valve is placed in the passageway connecting it with the cylinder. The Keine Indicator* has been developed accordingly for the continuous indication of the maximum values of Diesel engine combustion pressures. The makers co-operated in providing the special features required for the fitting of the instrument to the C.F.R. engine for the measurement of a wide range of maximum pressures including the exceptionally high pressures accompanying early preignition. These have frequently been of the order of 1800 p.s.i.

The passageway from the check valve to the cylinder, which must be surrounded by a length of cooling fins, was of the minimum practicable diameter, namely 1/16 *in.*, in order that the volume would be small relative to that of the combustion chamber of the C.F.R. engine at exceptionally high compression ratios. The check valve was especially designed to withstand the high temperatures and pressures accompanying preignition while maintaining accuracy of seating. A special valve of a double seating type was supplied for the closure of the connection from the cylinder to the check valve in order that the indicator

* *Keine Diesel Accessories Inc. 10352 Pacific Ave., Franklin Park, Ill., U.S.A.*

might be used in the course of a trial only as required. When the indicator was used for experiments described in this Part, maximum combustion pressure was observed after C.R. had been adjusted to the apparent optimum value, which was then corrected for the volume of the passageway connecting the indicator to the cylinder. The results of a typical set of experiments made with heptane as the fuel, charge density being 64% of normal, are given by the graphs of Fig. 14.

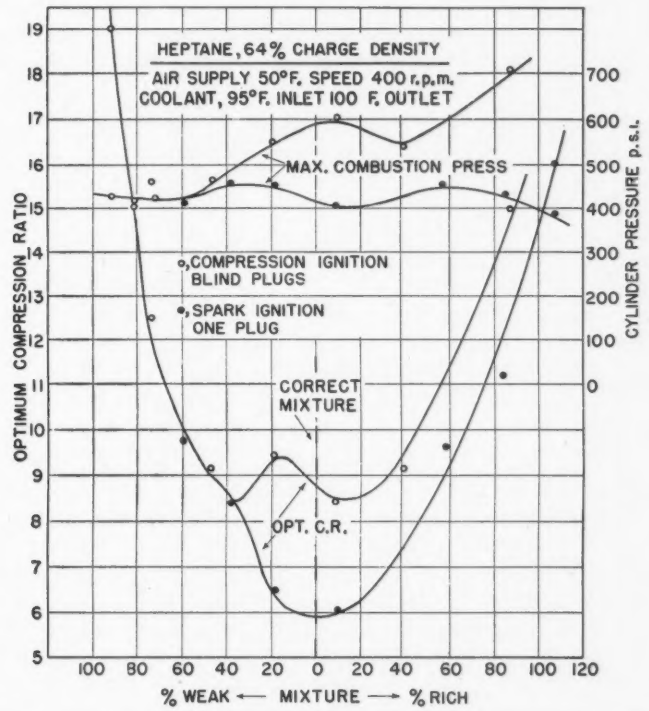

HEPTANE, 64% CHARGE DENSITY
AIR SUPPLY 50°F. SPEED 400 r.p.m.
COOLANT, 95°F. INLET 100 F. OUTLET
MAX. COMBUSTION PRESS
o, COMPRESSION IGNITION BLIND PLUGS
•, SPARK IGNITION ONE PLUG
CORRECT MIXTURE
OPT. C.R.
OPTIMUM COMPRESSION RATIO
CYLINDER PRESSURE p.s.i.
% WEAK ← MIXTURE → % RICH

FIG. 14. Maximum combustion pressure at Opt. C.R. with compression ignition at 10° before t.d.c. Heptane–air mixtures, 64% of normal charge density.

The characteristics of maximum combustion pressures as exhibited by the graphs of the figure are as would be expected from the results of ignition experiments described earlier in this Part and from considerations based on the nuclear theory of ignition, and it is shown by the graphs that maximum combustion pressures for mixtures leaner than 50% weak have the same value with or without spark ignition. On the other hand, maximum combustion pressures for very rich mixtures increase rapidly as M.S. is further increased if ignition is by compression, but decrease when ignition is by spark, as would be expected from the results of corresponding compression and spark ignition experiments given by the graphs of Fig. 12.

The ignition by compression of rich mixtures, which tend to run "cool" in an engine, requires a relatively high C.R. for the formation of the concentration of nuclei necessary for ignition, and rate of flame propagation after ignition occurs must be correspondingly rapid. Thus an explanation is afforded for the extremely high maximum pressure and the accompanying heavy combustion knock, observed in the circumstances.

The experimental results for maximum combustion pressures can be applied to correlate charge density and knock intensity. The charge density, in terms of volumetric efficiency, was 64% of the normal 85%, that is, it was 54% of the 100% volumetric efficiency which would require some degree of supercharging for its attainment. It can be assumed that absolute combustion pressures increase directly with increase in charge density if the effect of surface temperatures be neglected. Thus considering the correct mixture, maximum combustion pressure with spark ignition was 425 p.s.i., absolute; an experimental value which includes pressure losses due to reactions depending on the increase of temperature. Therefore, at the normal volumetric efficiency of 85% and in accordance with the assumption mentioned, maximum combustion pressure would have been 665 p.s.i. (gauge), and 775 p.s.i. (gauge) at 100% volumetric efficiency. Similarly, when ignition was by compression, Opt. C.R. being 8.8, the experimental value of maximum combustion pressure was 590 p.s.i. (gauge) and the respective maximum values would have been 955 and 1115 p.s.i. (gauge) at 85 and 100% volumetric efficiency, if it were then possible to adjust C.R. to an optimum value.

An estimate of the knock intensities corresponding to the maximum combustion pressure mentioned above can be made by reference to the graphs of Fig. 2. Thus it will be seen, for example, that when using a 10% rich heptane–air mixture at 64% of normal charge density, the Opt. C.R. being 8.65, knock intensity was described as "medium". The maximum combustion pressure in the circumstances, according to the corresponding graph of Fig. 14, was 600 p.s.i. It is evident, therefore, that if charge density were increased even to the normal value, maximum combustion pressure would be expected to increase to 955 lb. p.s.i. and an investigation of the characteristics of compression or nuclear ignition would be prevented by the severity of combustion knock.

Lower Limit of Inflammability, Pentane

It has been shown that in the conditions used for experiments with pentane, hexane, and heptane, described in this Part, spark ignition becomes ineffective for mixtures leaner than approximately 45% weak but that a wide range of still leaner mixtures are ignitable by compression; an effect attributed to nuclear ignition. Thus the experimental results, Fig. 8, show that when pentane was used as the fuel for the C.F.R. engine, charge density being 64% or normal, it was possible to reduce mixture strength until brake horsepower became nearly zero, provided C.R. were adjusted continuously to the optimum value. Although M.S. was then 74% weak it was apparent that the lower limit of inflammability had not been attained.

The first attempt to determine the possible lower limit was made at a time when cylinder wear had become excessive. The results were however of considerable interest and are given by the graphs of Fig. 15. B.H.P. became zero when the pentane–air mixture was 81% weak. I.H.P. was then 0.58, which is the H.P. required to overcome friction and pumping losses. Then by using the dynamometer to supply power to compensate in part for the losses, it became possible to reduce M.S. to 96% weak and I.H.P. to 0.07. The dynamometer then supplied 0.54 H.P. leaving 0.07 H.P. to be supplied by combustion of the fuel. It was a small margin but appeared to be real, because engine speed decreased when the fuel supply was stopped and an increased supply of power by the dynamometer was then required to maintain the speed at 400 r.p.m.

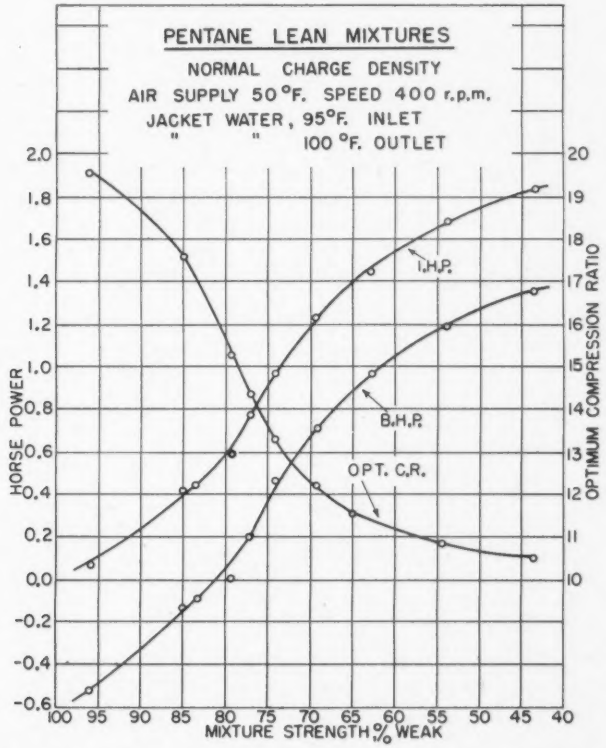


FIG. 15. Results of experiments with pentane–air mixtures leaner than 40% weak, made to determine lower limit of inflammability. Ignition by compression, no spark plugs. Normal charge density.

The mixture 96% weak contained 4% of the fuel required for the correct air to pentane ratio of 15.3:1, by weight. Ignition was therefore obtained with an air to pentane ratio of approximately 370:1 by weight.

Limits of inflammability are given usually in terms of the percentage of the vapor of the combustible in a mixture with air. Thus the lower limit of inflammability of a pentane–air mixture ignited by a spark at atmospheric pressure is given by Coward and Jones (1, p. 125) as 1.4. The mixture is then 45% weak and it will be remembered that spark ignition in the engine failed when M.S. was reduced so that it was approximately that value, no allowance being made for the effect of temperature and pressure or for the effect of dilution of the mixture with residual gas. It is possible that one effect compensated for the other.

The ultimate lower limit, attained by compression ignition when the pentane–air mixture was 96% weak, was 0.104 as compared with that of 1.4 given by Coward and Jones for ignition by spark.

The accuracy of the results for the ultimate lower limit may have been affected by the combustion of lubricating oil. The engine, as already mentioned, was not in first class condition and a thin oil, S.A.E. 10 — 10W, was used in order to reduce piston friction in the cool conditions of operation. The engine was, however, not "running on oil" even when M.S. was nominally 96% weak because speed diminished when the pentane supply was stopped. It is nevertheless indicated by the unusual double inflection in the graph, Fig. 15, for the relation between Opt. C.R. and M.S., that the oil may have constituted an appreciable part of the combustible mixture when it was leaner than 85% weak.

Lower Limit of Inflammability, Heptane

The experiments were made with mixtures leaner than 40% weak. It was possible, therefore, to use normal charge density and thus obtain a greater power output for a particular M.S. than when charge density was subnormal, with a corresponding improvement in regularity of combustion as the lean mixture limit was approached. Special care was taken to reduce the quantity of oil passing into the combustion chamber by using a cylinder and piston in nearly new condition and by fitting new rings to the piston.

Experimental results are given by the graphs of Fig. 16, for the relations between M.S. and Opt. C.R., indicated thermal efficiency, I.H.P., and B.H.P. A maximum value of 42% was obtained for indicated thermal efficiency at a M.S. of approximately 68% weak. B.H.P. was zero at a mixture 84% weak and I.H.P. was then 0.45. The leanest mixture with which continuous operation was possible was 93% weak and Opt. C.R. was then 22.8 and the corresponding lower limit of inflammability was 0.133 as compared with the value of 1.0 given by Coward and Jones (1, p. 125) for a heptane–air mixture ignited by a spark at atmospheric temperature. A mixture 93% weak contains air to fuel in the ratio of 220:1 by weight.

Decomposition Products of Fuel Which Remain on Surfaces of the Combustion Chamber

Nuclei of ignition dispersed throughout the combustible mixture consist, according to the modified nuclear theory of ignition (2), of the products of the thermal decomposition of the fuel. The nuclei are necessarily molecular aggre-

gates and may be assumed to vary in size especially when concentration of fuel in the mixture with air is not uniform. It is to be expected that the smaller ones could be oxidized without liberating sufficient heat to start a flame and that some proportion only of the larger ones would survive combustion. These, in large proportion, would be carried out with the exhaust but some might remain as deposits on relatively cool surfaces in the combustion chamber. These deposits when found in the combustion chamber can be attributed to decomposition of the fuel solely if the cylinder, piston, and rings are in such good condition that the least possible amount of lubricating oil passes into the combustion chamber. This condition is of the utmost importance when an endeavor is made to observe deposits remaining after the use of mixtures containing fuel in extremely small concentration.

Inspections of deposits remaining in the combustion chamber were always made after ignition had been by compression, with blind plugs used in place of the spark plugs and the bouncing pin and when compression ratio had been adjusted to the optimum value for any particular M.S. Engine speed was always 400 r.p.m.; air supply temperature 50°F. and jacket coolant 95 to 100°F.

The first series of inspections was made when heptane was being used as the fuel with a charge density 78% of normal. After a 60% weak mixture had been used for a period just long enough to obtain steady running conditions, the water cooled surfaces of the combustion chamber were found to be coated with a brown deposit. It was little more than a color which could be wiped off easily from the smooth surfaces of the blind plugs, but appeared again after the briefest possible running period. The color did not appear on the warmer surface of the piston, which remained clean and dry. No other type of deposit was observed on increasing mixture strength until Opt. C.R. had passed through the first minimum value of 8:1, see Fig. 7., and attained the intermediate maximum of 9.4. The mixture was then 20% weak and observation disclosed the presence on the piston crown of scattered particles of carbon which reflected light from the inspection lamp and patches of carbon on the blind plugs. The next inspection, made after using the correct mixture, for which the second minimum Opt. C.R. occurred, disclosed a very thin and patchy layer of black carbon on the piston crown and a nearly uniform layer on the blind plugs. The layers became uniform and increased in thickness as M.S. was further increased. The carbon was always of the nonadherent type and black smoke appeared in the exhaust.

The immediate deposition of a brown color on relatively cool surfaces in the combustion chamber was of especial interest in that the phenomenon could not well be attributed to the decomposition or oxidation of lubricating oil. The engine was therefore dismantled, cleaned, and run for three hours with the mixture 60% weak. The first inspection made after running conditions had become steady disclosed that, as before, the brown color had appeared on relatively cool surfaces. It was especially evident on the blind plugs which could be removed for close inspection. The brown color appeared on the piston crown also, as the trial progressed, and at the end of the period of three hours a granular deposit which could be scraped but not blown off had formed.

On completion of the experiments with heptane made to determine the lower limit of inflammability at normal charge density, Fig. 16, the piston crown was found to be coated with a granular brown deposit, the water cooled surfaces and the inlet valve with a thin brown deposit and the exhaust valve with a thin white deposit. These experiments were begun with a mixture 40% weak and it seemed, therefore, that the deposits observed after the mixture had been reduced to 93% weak at the conclusion of the experiments might be residuals from deposits formed in the early stages of the experiments.

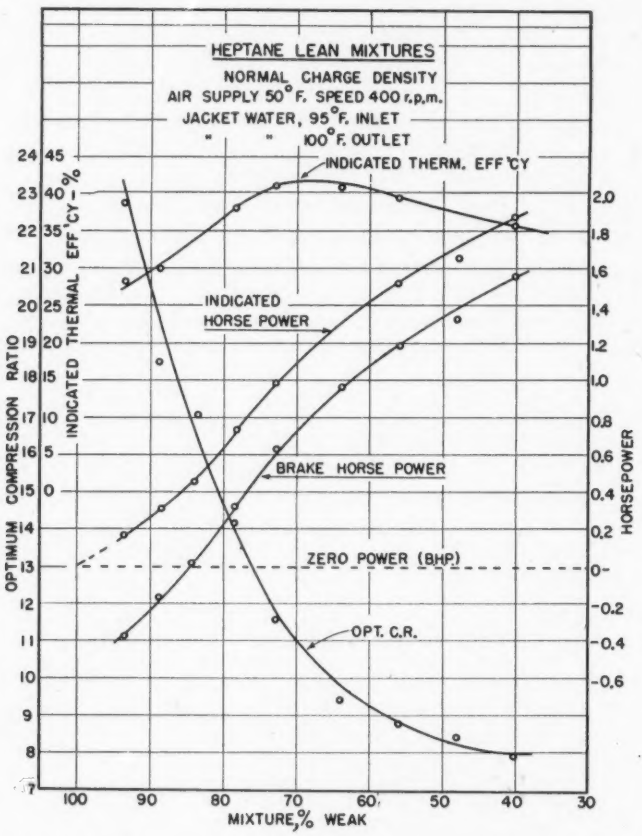


FIG. 16. Results of experiments with heptane–air mixtures leaner than 40% weak, made to determine lower limit of inflammability. Ignition by compression, no spark plugs. Normal charge density.

It was decided, therefore, to *begin* a set of experiments with an extremely weak mixture and after the engine had been given a complete "top overhaul" it was run for two hours with a pentane–air mixture 65 to 70% weak. An inspection made at the end of the period disclosed that the exhaust valve was coated with

an extremely thin layer of a nearly white substance and that all other surfaces were clean. The M.S. was then increased to be 45 to 50% weak and the engine run for a period of four and one-half hours. The cylinder was then removed for a close inspection of all the combustion chamber surfaces. The blind plugs and portions of the other directly cooled surfaces were found to be coated with a dark brown substance, partly globular. There was a dark brown color on the inlet valve and the exhaust valve, as before, was thinly coated with a nearly white substance. The piston crown was thinly coated with a brown substance of a sticky and apparently resinous nature.

Deposits from the decomposition and oxidation of lubricating oil cannot occur in the M.I.T. compression ignition machine; nevertheless it was found by C. F. Taylor and associates (8, p. 241) that "in normal use the cylinder head and piston acquired a dark brown color. No attempt was made to remove this film except to wipe the surface with a clean linen cloth". In the course of experiments made earlier with the M.I.T. machine (7, p. 6), it was found that soot of a fine gossamer texture was deposited in the combustion chamber after explosion of rich isooctane mixtures.

Tizard and Pye (9, p. 115) when using a single stroke machine with a compression time of 0.14 sec. which is over 20 times longer than that of the M.I.T. machine, but regarded as "small" at the time, found that on compressing hydrocarbons and ether to temperatures well above that of ignition, carbon was thrown down even though oxygen was in excess. It was not recognized that the carbon was a product of the decomposition of the fuel. Their explanation that it was the result of preferential burning of the hydrogen of the molecules is not acceptable in view of the greater heat energy required to break the C–H than the C–C bonds.

The Effect of Engine Heat Load on the Characteristics of Ignition and Combustion

The combustible mixture entering the cylinder of a carburetor type engine in a state of high turbulence is brought into contact during induction and compression with surfaces that have been raised to relatively high temperatures by previous exposure to flame. The surface temperatures attained in steady running conditions depend on the heat load; defined as the heats of compression and combustion not converted into work or rejected with the exhaust. The surface temperatures attained accordingly vary with M.S. and C.R. if the other controlling factors, namely, engine speed, charge density, and the temperatures of the jacket coolant and the air supply remain constant. The surface temperatures would have maximum values at any particular C.R. when the mixture is correct. The surface of maximum temperature is probably that of the ceramic core of a "hot" variety of spark plug. That of the exhaust valve may be expected to attain a lower temperature and that of the central part of the piston crown a temperature still lower.

The "new method" of experiment is based on the "other factors" being selected to provide the minimum practicable heat load in an engine developing power, thus its effect on combustion characteristics can be shown only by

increasing it. An increase can be obtained by increasing engine speed but the experimental results would then not be comparable with those obtained at the speed of 400 r.p.m. selected as one of the standard conditions of the new method of experiment because the change of speed would not change heat load only. The heat load could be increased by increasing charge density but it would then not be possible to adjust C.R. to an optimum value over the range of M.S. which included the correct value because of the consequent severity of combustion knock. Experiments to demonstrate the effect of an increase of heat load were therefore made without change of conditions other than those of temperature. Thus the temperature of the jacket coolant was raised from a maximum of 100°F. to 212°F. and the mixture temperature raised to 300°F. These are the temperature conditions of the C.F.R.–A.S.T.M. motor method of knock rating.

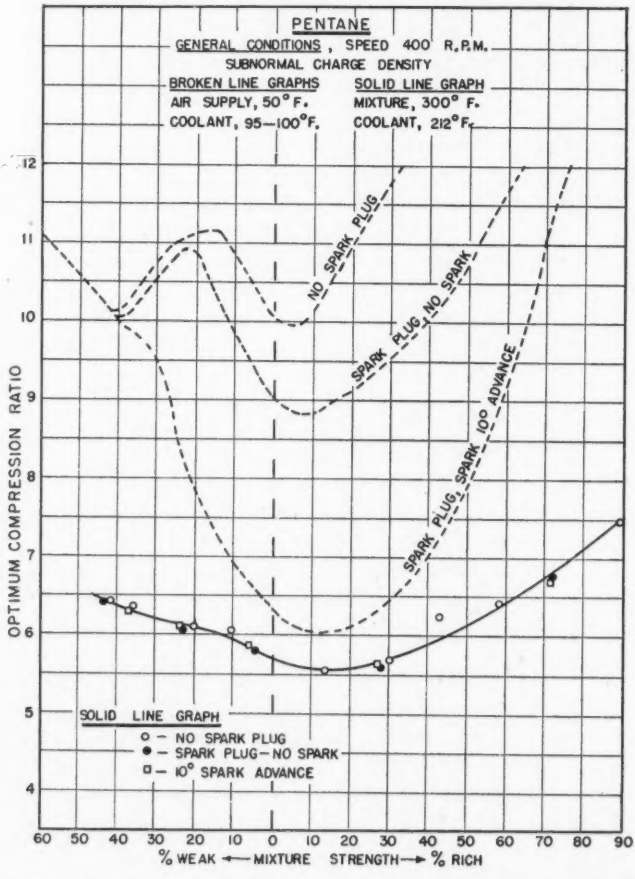


FIG. 17. Experimental results showing that on increasing heat load, the relation between Opt. C.R. and M.S. becomes independent of whether ignition is by compression with or without an unfired spark plug or by spark 10° before t.d.c. Pentane–air mixtures, subnormal charge density.

The experimental results obtained with the increased heat load, when using pentane as the engine fuel, are given by the solid line graph of Fig. 17. The broken line graphs of the figure are reproduced from Fig. 11, and are for results obtained with the relatively low heat of the new method of experiment. It is shown by the results given by the solid line graph that with combustion chamber surfaces at the temperatures due to a high heat load, the values of Opt. C.R. and necessarily the corresponding maximum values of thermal efficiency and power were obtained irrespective of the method of ignition. The broken line graphs show that with the relatively low heat load, which is an essential feature of the new method of experiment, it is possible to investigate on a comparable basis and over a wide range of mixture strength the separate effects on thermal efficiency and power of ignition by compression with and without an unfired spark plug in place and of ignition by spark.

The results of heat load experiments made when using heptane are exhibited by the graphs of Fig. 18. They are similar to those of Fig. 17 for pentane except that with the high heat load Opt. C.R. over the mixture range 30% weak to 30% rich, for compression ignition with no spark plugs in place, was somewhat higher

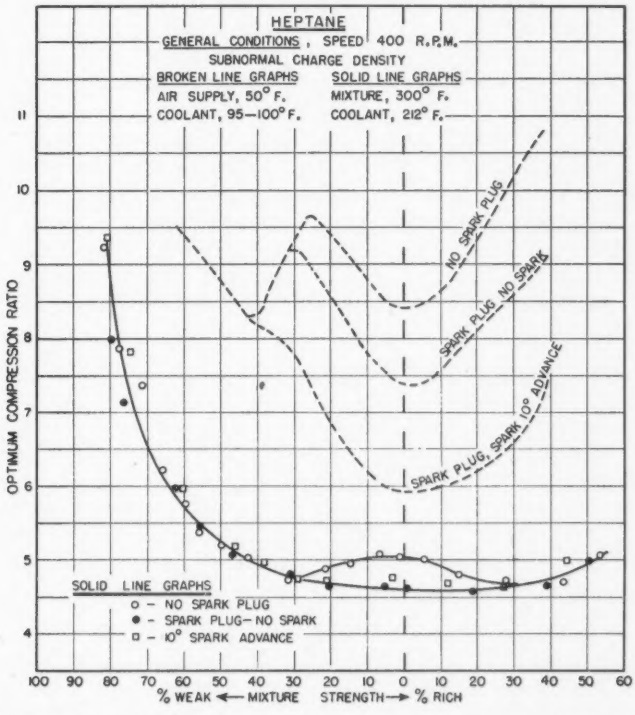


FIG. 18. Experimental results showing that on increasing heat load, the relation between Opt. C.R. and M.S. becomes nearly independent of whether ignition is by compression with or without an unfired spark plug or by spark 10° before t.d.c. Heptane–air mixtures, subnormal charge density.

than with one unfired plug or with ignition by spark. The difference was a maximum of 0.5 C.R. at correct mixture strength and indicates the beginning of a W form of graph. It is probable, in view of the experiments with spark ignition, Fig. 12, that lower values for Opt. C.R. with spark ignition would have been obtained if spark advance had been greater than the 10° used for the experiments. A further point of interest is that with subnormal charge density, a correct heptane–air mixture can be used at the Opt. C.R. of 4.5 even in the temperature conditions of the C.F.R.–A.S.T.M. motor method of knock rating.

DISCUSSION

The C.F.R. carburetor type engine became a compression ignition machine when operated in the conditions of the new method of experiment. The characteristics of combustion then obtained when using heptane, hexane, and pentane as engine fuels are similar to those described in Part XIX (6) with reference to experiments with acetaldehyde and diethyl ether. It was thus possible, with all five fuels, to operate the engine with ignition by compression over an extremely wide range of M.S. The graphs relating Opt. C.R. and M.S. were always of a W form when ignition was by compression and ignition by spark always failed for mixtures leaner than those within the range 40 to 50% weak. Moreover, it is obvious from the W form of the graphs that the relation between Opt. C.R. and thermal efficiency as affected by M.S., which was discussed at some length in Part XX (3) with reference to experiments with acetaldehyde and diethyl ether, is of the same character in respect of the normal paraffin fuels used for the experiments of this Part. The relation is of fundamental importance concerning the nuclear theory of ignition, the cause of detonation, and the mechanism of combustion in Diesel engines and will be discussed in a subsequent Part after some further investigation has been completed. It is possible, however, to state that the experiments with the normal paraffins indicate, as was shown by those with acetaldehyde and ether, that the departure of indicated from ideal values of thermal efficiency depends in part on the endothermic decomposition reactions required to produce nuclei of ignition in the combustible mixture of fuel and air.

Discussion will be concerned at present with other characteristics of combustion developed in the course of the experiments described in this Part and with the respective advantages for combustion research of the carburetor engine used as a compression ignition machine and the single stroke compression ignition machine. References will be made accordingly to the published data obtained by C. Fayette Taylor and associates (8) when using the single stroke machine developed by them in the Massachusetts Institute of Technology. These references will, for the sake of brevity, be to the "M.I.T. Machine".

Compression Ignition Conditions in the Engine and in the Single Stroke M.I.T. Machine

The engine, regarded as a compression ignition machine, differs from the single stroke variety as follows:—

The combustible mixture in the engine is diluted with exhaust gas to an extent depending on C.R. and the "delay period" must be considered as beginning before, instead of being taken as beginning at the end of, compression

in the machine. The combustible mixture is highly turbulent at the beginning of compression in the engine and is not so at any time in the single stroke machine.

Surface temperatures in the engine are less uniform than in the single stroke compression ignition machine mainly because the temperature of the necessary exhaust valve rises above that of other surfaces to an extent depending on the heat load which varies with M.S. and C.R., other conditions being unchanged. Thus the combustible mixture entering the engine is brought into contact with nonuniformly heated surfaces for the 360° of crank angle which may be taken as required for the induction and compression of the charge and represents a time of 0.15 sec. when the engine speed is 400 r.p.m. There is no induction stroke in the machine and surface temperature may be taken as uniform at the beginning of compression which, in the M.I.T. machine, generally occupied a time of 0.006 sec. and was therefore nearly adiabatic (7). An equal time of compression in the engine would require a speed of $400 \times \frac{0.075}{0.006} = 5000$ r.p.m. The delay period in the M.I.T. machine, as in other compression ignition machines, is taken as beginning when compression is completed, that is, while the temperature and pressure of the reacting mixture are falling slowly from the maximum value attained. The delay period is therefore measured as if an engine running at 5000 r.p.m. were suddenly stopped at the finish of the compression stroke and held immobile until reaction starting in the compressed mixture did or did not lead to ignition. The delay period in an engine used as a compression ignition machine must be taken as ending prior to the completion of compression if combustion is to occur at nearly constant volume.

The characteristics of ignition by compression can be related to thermal efficiency and power when the engine is used as a compression ignition machine and by adjusting C.R. to an optimum value a rational basis is obtained for the relative tendencies of detonating fuels to autoignite when used at any particular M.S.

The single stroke machine as developed in the M.I.T. possesses the important feature that, after ignition occurs, the progress of the flame can be recorded photographically. The novel method of sealing the piston of the machine is effective and lubricating oil is not required. When the C.F.R. engine is used as a compression ignition machine, especially at the relatively low speed of 400 r.p.m., experimental difficulties arise from gas leakage at extremely high compression ratios and from the passage of lubricating oil into the combustion chamber. It was possible to obtain repeatable and significant experimental results solely by exercising the utmost care to keep the cylinder, piston, and rings in nearly new condition at the expense of much time and frequent replacement of parts.

Optimum C.R., Preignition, and Limit of Power Output, With Compression Ignition

The graphs of Figs. 1 and 2 illustrate the method used to determine Opt. C.R. and its variation with mixture strength. It had been assumed, prior to the

taking of indicator diagrams, that on adjusting C.R. to obtain maximum power output at a particular M.S., maximum combustion pressure would be attained at approximately 10° after t.d.c. The diagrams of Figs. 3 and 5 justify the assumption. Those of Fig. 3 show how the time of occurrence of maximum combustion pressure advances as C.R. is raised, and indicate accordingly that "preignition" may be defined as any igniting effect which causes maximum combustion pressure to occur earlier than 10° after t.d.c. *The extent to which this definition can be applied generally remains to be determined.*

The compression ignition experiments were carried out over the range of M.S. for which B.H.P. varied from zero to a maximum value. The graphs of Figs. 1 and 2 show that maximum power output was obtained with a M.S. approximately 10% rich when using heptane or hexane. Power output could not be increased by increasing either the M.S. or the C.R. An increase in either of these factors merely increased the rate of decomposition of fuel as was shown by an increase in carbon deposit in the combustion chamber and an increase in the density of black smoke in the exhaust.

The Delay Period With Ignition by Compression

The indicator diagrams of Fig. 3 are for a mixture 70% weak. They show that the beginning of the delay period advances and the length diminishes as C.R. is raised. It is difficult to determine the exact time of the beginning because it may not be accompanied by a pressure change other than that due in part to the increasing compression pressure. However, judged by pressure rises, it appeared to begin to approximately 10° before t.d.c., diagram No. 1, Fig. 3, and to advance by 3° only to 13° before t.d.c., diagram No. 4, the C.R. having been increased from 10 to 12.8. The length of the period, reckoned accordingly, decreased from 20° to only 4°. The rate of change diagram, Fig. 4, provides some further information in respect of the delay period. Thus the sudden increase in dp/dt at 8° before t.d.c. corresponds to the beginning of a first or preliminary stage of combustion as shown by diagram No. 2 of Fig. 3 but the preceding horizontal part of the diagram, Fig. 4, indicates that reaction began in the mixture at least 20° before t.d.c. Thus a determination of the length of the delay period, when using the engine as a compression ignition machine, presents some difficulty whereas it is a simple matter with the single stroke compression ignition machine if it is reckoned from the completion of compression. It is, however, shown very clearly by the engine experiments that the length of the delay period decreases as C.R. is raised, and it is of interest that a similar effect was shown by experiments with the M.I.T. single stroke machine, see conclusion No. 2 (8, p. 269).

Conclusion No. 1 of the reference quoted is that the "longest delays are observed at very lean or very rich mixtures". It is important to note that this conclusion is based on experiments made at constant C.R. with mixture strength varied and on reckoning the delay period as beginning on completion of compression. Engine experiments with constant compression ratio and variable M.S. were not made.

Conclusion No. 6 of the reference quoted is that "at very lean or very rich fuel ratios, the explosion is relatively mild". This conclusion is as in No. 1, based on experiments at constant C.R. However, referring to the graphs of Figs. 1 and 2, it will be seen that knock intensity in the engine diminished, from that observed at correct mixture, with decreasing concentration of fuel in the mixture with air. The engine experiments were made over a wider range of weak mixtures than that used for experiments with the M.I.T. machine and when using heptane for the engine experiments, Fig. 2, running was smooth and regular with a mixture 71% weak and combustion was inaudible at the Opt. C.R. of 11.7. Even on increasing C.R. to 14.1 to obtain sufficient preignition to reduce power output to zero, combustion knock was "light" only. There was always a considerable intensity of combustion knock when using rich mixtures but little increase as M.S. was increased and C.R. raised to maintain an optimum value. Thus it may be concluded that similar results were obtained by the engine and the M.I.T. machine although conditions were not quite comparable. The first part of conclusion No. 9 of the reference quoted above is that "the autoignition of *n*-heptane sometimes proceeds in two stages especially at lean fuel–air mixtures". The engine experiments exhibit a similar but more pronounced effect, thus the pressure–time indicator diagrams, Fig. 3, for mixtures 70% show two-stage ignition very clearly and the rate of change diagram, Fig. 4, shows the stages in quite a striking manner. Single-stage ignition only is shown by the pressure–time diagram, Fig. 5, for a nearly correct mixture. Thus results obtained with the engine are again in agreement with those obtained with the M.I.T. machine. The second part of conclusion No. 9 deals with the effect of tetraethyl lead (T.E.L.) on the delay period. Results of comparable engine experiments are not yet available.

The Relations Between Opt. C.R., M.S., Brake and Indicated Horsepower, and Brake and Indicated Thermal Efficiency

The method of determining the Opt. C.R. for any particular mixture strength as shown by the graphs of Figs. 1 and 2 was used to obtain the relation between Opt. C.R. and M.S. for mixtures with air of pentane, hexane, and heptane. Experimental results are given by the graphs of Fig. 6 for a charge density of 64% of normal and by those of Fig. 7 for a density of 78% of normal. The graphs are of a W form with two minimum values of Opt. C.R. and an intermediate maximum. Thus it is confirmed that when ignition is by compression, with the spark plugs replaced with blind plugs, the relation between Opt. C.R. and mixture strength for the three paraffins is similar to that obtained when acetaldehyde and diethyl ether were used as fuels in the same circumstances, see *B* graphs, Figs. 3 and 4, Part XIX (6).

The second minimum value of Opt. C.R. always occurred within the maximum power mixture strength range, namely, correct to 20% rich. The corresponding minimum value of the Opt. C.R. may therefore be taken as an approximation to the highest useful compression ratio (H.U.C.R.) in the conditions of the

experiments. The five fuels for which data are available from experiments at a particular charge density, namely 64% of normal, can then be rated as below:

	H.U.C.R.
Diethyl ether	4.8
Acetaldehyde	5.6
Heptane	8.3
Hexane	9.8
Pentane	10.0

Knock ratings can be determined in the conditions of the relatively high heat load of the C.F.R.–A.S.T.M. motor method of knock rating for the hexane and pentane only. The other fuels are not usable at maximum power M.S. in the temperature and charge density conditions, at compression ratios higher than the lower limit of the engine.

The relations between Opt. C.R., M.S., I.H.P., and B.H.P. are given by the graphs of Fig. 8; those between Opt. C.R., M.S., and indicated and brake thermal efficiency are given by the graphs of Fig. 9. The graphs are for the results of experiments with pentane–air mixtures. It will be noted that when C.R. was continuously adjusted to the optimum value, it was possible to continue reducing mixture strength until B.H.P. became zero. The mixture was then 75% weak. Similar experimental results were obtained when using mixtures of air with heptane or hexane. It is obvious from an inspection of the graphs and from the results of similar experiments with acetaldehyde and diethyl ether described in Part XX (3) that power and efficiency do not vary with compression ratio in the conventional manner, as mixture strength is reduced. This aspect of the experimental results involves consideration, as in Part XX (3), of the adverse effect on thermal efficiency due to the endothermic reaction required to produce nuclei of ignition and will be discussed, as mentioned earlier, together with the results of further experiments, in another Part.

The Igniting Effect of an Unfired Spark Plug

The results of experiments with acetaldehyde and diethyl ether, described in Part XIX (6) indicated that an igniting effect might be attributed to an unfired spark plug but relevant experiments were not made. The igniting effect again became apparent when paraffin fuels were used for the experiments of this Part and its magnitude and certain of its characteristics as determined by experiments with heptane and pentane made at 78% of normal charge density are exhibited by the graphs of Figs. 10 and 11. Thus it will be seen by reference to the graphs that the igniting effect became evident after M.S. had been increased to be greater than that corresponding to the first minimum value of Opt. C.R. When mixture strength was further increased to the correct value, the magnitude of the igniting effect was represented by decreases of 1.5 and 1.0 in the values of Opt. C.R. for mixtures with air of heptane and pentane, respectively.

The experimental results given by the graphs of Fig. 15 show that the igniting effect of the unfired spark plug must be attributed to the ceramic core, not to the

points. It may safely be assumed, however, that the core cannot have become hot enough in the low temperature conditions of the experiments to cause the direct surface ignition commonly described as preignition. Such an effect would not be subject to the precise control by C.R. over a wide range of M.S., shown by the graphs of Figs. 10 and 11 and by the results of other relevant experiments.

The igniting effect of the spark plug core is explicable by the nuclear ignition–pressure wave theory discussed in Part XX (3, p. 59). Thus compressed mixture in proximity to the core would attain a higher than average temperature and therefore be subject to preferential decomposition and consequent nuclear ignition. The explosive ignition of this relatively small part of the charge could initiate a pressure wave which on passing through the unburned part would complete decomposition progressively to the extent necessary to provide the concentration of nuclei required for its ignition.

When the unfired spark plug was replaced by a blind plug, it was necessary to raise the compression ratio in order to obtain ignition. The effect is shown by the graphs of Figs. 10 and 11 and is attributed to the relatively high surface temperature of the exhaust valve. That is, the exhaust valve, in the absence of the hotter spark plug core, may provide the heat required for the preferential decomposition and consequent nuclear ignition of adjacent mixture.

The Spark Ignition Delay Period

A carburetor type engine using ordinary liquid paraffinic fuels is operated in practice with ignition by spark and with the C.R. having a fixed value sufficiently low to avoid detonation. The temperatures and pressures attained prior to inflammation, even by the end gas, are then insufficient for the decomposition of the fuel, in the time available, to the extent necessary for nuclear ignition. In these circumstances a pressure rise due to combustion of the fuel does not occur until 10 to 12° of crank angle after passage of the spark and as mixture strength is reduced to become leaner than approximately 20% weak, rate of flame propagation becomes so low that combustion cannot be completed before expansion begins and may continue during the expansion and exhaust strokes. The consequences are that the exhaust valve may be damaged by overheating and the fresh charge ignited when the inlet valve opens. It is well known that these effects tend to occur in multicylinder engines because of uneven distribution of fuel. A single cylinder engine will cease to develop power before damage occurs.

It is important to remember that the experimental results given in this Part, except those shown by Figs. 1 to 3, are always for optimum values of C.R. and that it has been shown by indicator diagrams that maximum combustion pressure then occurs at approximately 10° after t.d.c. for any value of M.S.

Referring now to the experimental results for spark ignition, Fig. 12, it will be seen that when a correct mixture was used, it was necessary to raise Opt. C.R. from 5.45 to 6.25 on retarding the spark from 20° to 5° before t.d.c. When a mixture 20% weak was used, it was necessary to raise the Opt. C.R. from 6.05 to 8.1. When, however, a mixture 20% rich was used, it was necessary to

raise Opt. C.R. from 5.8 to 6.8. That is, in order that maximum combustion pressure would occur at 10° after t.d.c. when spark ignition was retarded from 20 to 5° before t.d.c., it was necessary to increase Opt. C.R. by 0.80 ratio at correct M.S., by 2.05 ratios at a M.S. 20% weak and by 1.0 ratio at a M.S. 20% rich. These results are in accordance with the view that as C.R. is raised to maintain an optimum value as spark timing is retarded, the necessary increase in rate of flame propagation is due to an increase in the concentration of nuclear centers of ignition. The smaller increase of Opt. C.R. required for rich as compared with weak mixtures is attributed to the concentration of nuclei increasing with increase of mixture strength but secondary effects must be taken into account. Thus the heat load which affects the velocity of the decomposition reaction has a maximum value at correct mixture strength, approximately. The heat load diminishes on the weak side of correct M.S. with the decrease in the concentration of fuel in the mixture with air but it also diminishes on the rich side as the concentration of fuel in the mixture *increases* because of the consequent imperfect combustion and the reduction of temperature which always accompanies the use of overrich mixtures. Moreover this reduction of temperature may be due in part to the heat absorbed by the endothermic decomposition reaction which in the circumstances results in the profuse formation of carbon.

It is significant that as spark ignition is retarded, the graphs for the relation between Opt. C.R. and M.S. tend to assume the W form shown by the broken line graphs of Fig. 12 which were obtained when ignition was by compression at the relatively high values of Opt. C.R. required for decomposition of the fuel to the extent required for nuclear ignition.

CONCLUDING NOTES

The experiments described in this Part indicate the extent to which important characteristics of ignition and combustion can be investigated when the C.F.R. engine is used as a compression ignition machine. The results show that further experimental work would be profitable in respect of the following:—

(1) The nature of the nuclei formed by decomposition of the fuel, especially when very lean mixtures are used.

(2) The effect of decomposition reactions on thermal efficiency when knock resistant liquid hydrocarbon fuels are used.

(3) The temperatures of indirectly cooled surfaces such as exhaust valves and spark plug cores, as affected by heat load.

(4) The temperatures of the indirectly cooled surfaces that are required for ignition of the fuel–air mixture by direct contact and the nature of the products then formed by surface reactions.

(5) The temperatures of the indirectly cooled surfaces which are required for the initiation of a pressure wave in a mixture already sensitized to ignition by the products of a decomposition reaction and the rate of flame propagation in such a mixture.

(6) The inability of the electric spark to ignite mixtures leaner than approximately 45% weak as compared with the extension of an igniting effect to mixtures even leaner than 90% weak by compression ignition when fuels subject to nuclear ignition are used.

(7) The effect of heat load to limit the compression ratio usable with non-detonating fuels such as hydrogen, natural gas (methane), and manufactured gas.

Every item listed above can be regarded as a particular research project and the number could easily be increased. An investigation of even the items enumerated would be of interest concerning the mechanism of ignition and combustion in Diesel as well as in spark ignition engines and would probably add to present knowledge of the cause of explosions of combustible dusts and of the conditions required for the exceptionally rapid combustion of fuel–air mixtures in other than piston engines.

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SYNTHESIS OF POLYPEPTIDES AND THEIR ENZYMATIC HYDROLYSIS COMPARED WITH GLUTEN[1]

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ABSTRACT

Polymers of glutamic acid, lysine, and S-benzylcysteine were synthesized as well as the copolymers of these amino acids. The molecular weight of polyglutamic acid was determined by two types of end group analyses, namely—carboxyl, by glutamic acid decarboxylase, and amino nitrogen. The copolymer of glutamic acid and lysine was shown to be nonuniform on analysis of precipitated fractions. The action of pepsin–pancreatin enzyme combination on wheat gluten and the synthetic polymers was examined. Using acid hydrolysis as 100%, gluten was hydrolyzed 66%, the copolymer of glutamic acid, lysine, and cysteine, 25%; lysine–glutamic acid copolymer, 18%; while poly-S-benzylcysteine and polyglutamic acid were not hydrolyzed at all.

In studying the constitution of wheat gluten, it appeared that less complex synthetic polypeptides might be of value for comparative purposes. The production of N-carboxy acid anhydrides of amino acids and subsequent polymerization has provided an improved method of synthesis of polypeptides. By copolymerization of the monomers more complex polymers could then be prepared (13). Since gluten contains acidic and basic amino acids and important sulphydryl groups (17), the N-carboxy acid anhydrides of glutamic acid, lysine, and cysteine were synthesized. Various copolymers were then made and their homogeneity and molecular weight investigated. Finally a comparison of the extent to which gluten and the polymers could be hydrolyzed by proteolytic enzymes was made.

EXPERIMENTAL METHOD

Poly-S-benzyl-L-cysteine

Synthesis starting with cystine was abandoned when it was found that the N,N′-dicarbobenzyloxycystine intermediate, prepared by a modification of Bergmann and Zervas' method (4), was very difficult to crystallize. Since better crystalline derivatives of cysteine could be prepared and the active sulphydryl group was ultimately desired, cysteine was then used as the starting material. The active SH group was blocked by benzylation according to the method of Wood and du Vigneaud (23). The carbobenzyloxy derivative was then prepared essentially as outlined by Harington and Mead (15). The anhydride was synthesized as follows: S-benzyl-N-carbobenzyloxy-L-cysteine (8.0 gm.) was suspended in dry ether (60 ml.) and cooled in an ice–salt bath. Phosphorus

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pentachloride (5.6 gm., 15% excess) was added and the mixture shaken intermittently for an hour. After filtering through glass wool the ether was removed *in vacuo* at 40°-50° with careful exclusion of moisture. On addition of petroleum ether crystallization occurred. After three crystallizations from ethyl acetate, white needles of S-benzyl-L-cysteine N-carbonic anhydride were obtained, m.p. 99°-102°, decomposing at 136°-140°, yield 4.0 gm. (73%).

Poly-S-benzyl-L-cysteine was prepared by adding dry pyridine (8.0 ml.) to the above anhydride (2.5 gm.). After two hours the initial evolution of gas was over and the mixture was heated in a boiling water bath for two hours. The viscous dark product with a strong mercaptanlike odor was freed from pyridine and purified as a white powder by dissolving in hot methanol and fractionally precipitating by addition of increasing amounts of water. The polymer was soluble in acetic acid. A subsequent polymerization at room temperature over a 24 hr. period yielded a product with a less pronounced odor and insoluble in hot methanol and glacial acetic acid. End group analysis from total nitrogen and amino nitrogen indicated that the second polymer produced under milder conditions was of higher molecular weight. It was observed that during initial addition of pyridine to the anhydride a bright red color resulted. As polymerization proceeded the color changed to light brown and yellow.

Polyglutamic Acid

The first attempt to synthesize the polymer through the intermediate of chloromethyl carbonate and thionyl chloride as outlined briefly by Hanby *et al.* (11) was unsuccessful. A superior method as outlined subsequently by them was used and made use of benzyl chloroformate and phosphorus pentachloride (12). The γ-methyl-L-glutamic acid-N-carbonic anhydride was then polymerized in pyridine, saponified first with alcoholic potassium hydroxide, then with aqueous potassium hydroxide, and finally electrodialyzed to yield poly-L-glutamic acid. Purification of each intermediate was important to obtain maximum yields.

Poly-L-lysine

It was prepared according to the method of Katchalski *et al.* (14) from the monomer ε-carbobenzyloxy-L-lysine-N-carbonic acid anhydride described by Bergmann *et al.* (5). α, ε-dicarbobenzyloxy-D,L-lysine was also prepared, m.p. 104°-105°—its melting point could not be found in the literature. After treatment with phosphorus pentachloride, ε-carbobenzyloxy-D, L-lysine-N-carbonic acid anhydride was isolated. m.p. 92°-94°, decomposition 96°-98°. Differing from Katchalski, polymerization was done in dry pyridine.

Copolymers

I. Lysine and glutamic acid.—Freshly prepared N-carbonic anhydrides of ε-carbobenzyloxy-L-lysine (10.10 gm., 0.033 mole), and γ-methyl-L-glutamic acid (6.17 gm., 0.033 mole) were mixed thoroughly in the dry state and 40 ml. of dry pyridine added. The mixture was stirred until the evolution of gas became vigorous and then left to stand for 24 hr. The pyridine was removed *in vacuo* and the methyl ester saponified with 200 ml. 0.76*N* alcoholic potassium hydroxide at room temperature for 75 min., then at 0° for one hour. After washing the

solid with alcohol–ether and drying, the carbobenzyloxy group was removed by reduction with sodium in liquid ammonia. The excess sodium was then removed with ammonium chloride, the ammonia evaporated, and the dibenzyl washed out with ether. To lessen the amount of salt to be removed by dialysis, the polymer was precipitated by addition of hydrochloric acid to pH 5. The product which was white and formed large particles similar to coagulated protein was electrodialyzed and then subjected to fractionation as outlined below.

II. Lysine and cysteine.—This copolymer was synthesized in a similar manner to the above copolymer. The benzyl groups were removed by treatment with sodium in liquid ammonia and the hydrochloride of the polymer dialyzed. The resultant product when washed with alcohol and ether was light gray and had a strong mercaptan odor.

III. Glutamic acid and cysteine.—This copolymer was also prepared in a similar manner. After saponification and treatment with sodium in liquid ammonia the gray product had a strong mercaptanlike odor.

IV. Glutamic acid, lysine, and cysteine.—This copolymer was made as outlined above. After removal of the blocking groups, a white product was isolated with a faint mercaptanlike odor.

Molecular Weight Determination

During this investigation only the molecular weight of polyglutamic acid was studied in detail. Two methods were employed, both based on end group analysis. One involved determining the ratio of amino nitrogen to total Kjeldahl nitrogen. The other employed the use of the enzyme glutamic acid α-decarboxylase, where the total carbon dioxide liberated was compared with the total glutamic acid residues as measured by total nitrogen. The decarboxylase method as described by Schales *et al.* (18,19) measures the α-carboxyl groups and therefore only the terminal glutamic acid carboxyl in the polymer. Extracting the enzyme with phosphate buffer from squash was more satisfactory than extracting it from carrots. No interference was found from aspartic acid. Any racemization was indicated by a proportionally low evolution of carbon dioxide since the enzyme is specific for the L-isomer.

Since error in the end group analysis method is large, the results of the two methods can only be approximations. The amino nitrogen method indicated a molecular weight of 3300 or 24 glutamic acid units for the first polyglutamic acid synthesized. The result using glutamic acid α-decarboxylase indicated a molecular weight of 4100 or 31 units.

Table I contains the total nitrogen content by a micro-Kjeldahl method (16), amino nitrogen (20, 21, 22), and the average number of units per polymer calculated from these two values.

The copolymer of glutamic acid and lysine was examined for its homogeneity. It was found that the copolymer was soluble in alkali and as the pH was decreased, an increasing amount of precipitation occurred. Hydrolysis of fractions and the estimation of the glutamic acid–lysine ration would indicate any nonhomogeneity. The colorimetric method of Frame *et al.* (9) employing

TABLE I

AVERAGE NUMBER OF UNITS PER POLYMER UNIT

Polymer	% Total N	% Amino N	Average no. units/chain
Polyglutamic[1] acid	7·38	0·248	30
LGA[2]	5·05	1·77	37
LGB[3]	4·88	1·73	33
Polylysine	10·2	5·19	57
Poly-S-benzyl cysteine	5·23	0·261	21
Poly-S-benzyl cysteine	5·83	0·367	16
Polyglutamic acid – cysteine	6·72	0·467	14
Polylysine–cysteine[4]	7·62	2·83	18
Polyglutamic–lysine–cysteine[4]	10·2	2·92	21

[1] *Prepared later than the 24-unit polymer mentioned above.*
[2] *Polylysine – glutamic acid precipitated at pH 6.*
[3] *Polylysine – glutamic acid precipitated at pH 5.*
[4] *Since the end group method for molecular weight estimation could not be used when lysine was present in the copolymer the values were obtained by assuming that each copolymer contained an equal number of units of each of the amino acids in the polymer.*

sodium-β-naphthoquinone-4-sulphonate was used to determine both amino acids. Preliminary separation was accomplished using Deacidite, which was found more satisfactory than Decalso. Passage of the hydrolyzate through a column of Deacidite removed the glutamic acid. It was subsequently removed by eluting with N/4 hydrochloric acid. Table II includes the analysis of the glutamic acid–lysine polymer precipitated at pH 6 (LGA) and pH 5 (LGB).

TABLE II

GLUTAMIC ACID – LYSINE RATIO OF POLYMER FRACTIONS

Fraction	Mgm. amino acid/100 mgm. polymer		Ratio glutamic acid/ lysine
	Lysine	Glutamic acid	
LGA	36·8	26·8	0·728
LGB	32·5	29·3	0·905

In another phase of study a number of proteolytic enzymes were investigated for their hydrolyzing activity on wheat gluten. The amount of hydrolysis was determined by estimating the amino nitrogen evolved using the Van Slyke procedure (20, 21, 22) and comparing it with acid hydrolysis as 100%. To account for autodigestion of the enzyme, blank determinations were made using five times the enzyme concentration as substrate. The enzyme combinations studied included pepsin together with pancreatin (Takamine Co.), erepsin (from fresh hog mucosa), pepsin, a commercial erepsin, and wheat proteinase. A maximum hydrolysis of 66% was obtained with several enzyme combinations. These included pancreatin and, since this preparation was relatively uniform it was employed in subsequent studies on synthetic substrates. The final method,

similar to that used by Wooley and Sebrell (24), consisted of a preliminary 24 hr. digestion of 200 mgm. of substrate with pepsin (25 mgm.) at pH 1.5. The pH was then adjusted to 8.0 and pancreatin (50 mgm.) added. Digestion at 37° with shaking was continued for seven days.

The extent of hydrolysis of gluten and the various polymers and copolymers by the proteolytic enzyme combination mentioned above, as measured by amino acid liberation and compared to acid hydrolysis as 100%, is shown in the list below.

SUBSTRATE	PER CENT HYDROLYSIS
Gluten	66
Copolymer of glutamic acid – lysine–cysteine	26
Copolymer of lysine – glutamic acid	18
Polyglutamic acid	0
Poly-S-benzylcysteine	0

DISCUSSION

Using dry pyridine as the solvent medium for polymerizing the amino acid of glutamic acid, lysine, and cysteine, the molecular weight has been varied by the temperature of polymerization. More varied molecular weights have recently been reported by Coleman (7, 8), using alkali salts of weak bases and by others (2, 3, 12). Polymers of S-benzyl cysteine were synthesized for the first time as well as copolymers of cysteine, glutamic acid, and lysine. Since this work was completed, the synthesis of polylysine–glutamic acid has been reported (1).

In the estimation of the molecular weight of an amino acid polymer usually an analysis for only one end group is possible. Here advantage was taken of the specificity of α-glutamic acid decarboxylase, used here to estimate glutamic acid, to determine terminal α-carboxyl groups and thus afford a measurement of another end group. The molecular weight of polyglutamic acid was thus checked by these two end groups and the two values obtained agreed within the large experimental error of this method.

Gradual lowering of the pH of a solution of the copolymer of lysine and glutamic acid resulted in the isolation of fractions. Analyses of two of these for the two amino acids indicated that the polymer was nonuniform. As would be predicted, the glutamic acid – lysine ratio increased with the fraction precipitating at the lower pH.

A comparison of proteolytic activity on gluten and the synthetic polyamino acids indicated that the extent of hydrolysis decreased with decreasing complexity of the molecule with no hydrolysis of polyglutamic acid and poly-S-benzyl cysteine. Similarly Go and Tani got no hydrolytic cleavage with polyglycine and polyglycine leucine (10). On the other hand, Brand and Katchalski found that their polymer of polylysine was rapidly hydrolyzed in the presence of crystalline trypsin (6).

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